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Theoretical study on the addition reaction between propadienylidene and methyleneimine

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Abstract: The reaction mechanism between propadienylidene and methyleneimine was systematically investigated employing the second-order Møller–Plesset perturbation theory (MP2) method with the 6 – 31 + G* basis set. Geometry optimization, vibrational analysis, and energy property of the involved stationary points on the potential energy surface were calculated. The energies of the different species were corrected by single point energy calculations at the CCSD (T) // MP2 / 6 – 31 + G* level. From the surface energy profile, one important initial intermediate characterized by a 3-membered ring structure was located via a transition state firstly. After that, 3 different products possessing 3- and 4-membered ring characters were obtained through corresponding reaction pathways. In the first reaction pathway (1), a 3-membered ring alkyne compound was obtained. A 4-membered ring conjugated diene compound was produced in the other 2 reaction pathways, pathways (2R) and (2L). The energy barrier of the rate-determining step of pathway (1) is higher than those of the pathways (2R) and (2L), where the ultimate products of pathways (2R) and (2L) are more stable than that of pathway (1). Therefore, the dominating product of the addition reaction between propadienylidene and methyleneimine should be the 4-membered ring conjugated diene compound.

Key words: Propadienylidene, methyleneimine, reaction mechanism, MP2 method

1. Introduction

Carbenes can be defined as divalent carbon intermediates where the carbene carbon with 2 nonbonding electrons is linked to 2 adjacent groups by covalent bonds. It is well known that carbenes play an important role in organic chemistry, especially in addition reactions involving C = C and C = O double bonds.[1–3] Therefore, studies of carbenes have attracted much attention both from theoretical and applied chemists.[4–9]

C_3H_2 is a type of highly unsaturated carbene that is of great interest in the chemistry of carbon-rich gas-phase environments. As shown in Scheme 1, on its potential energy surface 3 isomers have been found. Propynylidene is the only one in triplet electronic ground state and the propadienylidene and cyclopropenylidene are in singlet state.[9–12] Moreover, all of them can be interconverted by photolysis.[13–15] The structure, thermochemical properties, and isomerization of C_3H_2 carbenes have already been investigated extensively.[9,16,17] It was found that the singlet cyclopropenylidene is the most stable isomer among the 3 species,[18–21] whose energy is lower than those of the propadienylidene and propynylidene.[22–25] Recently, the formation mechanism of the C_3H_2 carbene has been proposed by Goulay et al. using tunable vacuum ultraviolet photoionization and time-resolved mass spectrometry.[26]

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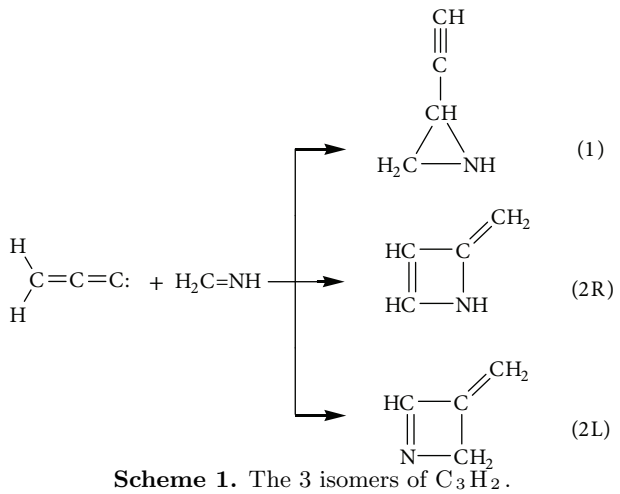

Scheme 1. The 3 isomers of C_3H_2.

Propadienylidene is the first member of the cumulene carbene series with great stability. It was produced in a laboratory discharge, whose rotational spectrum was determined precisely by Vrtilek et al.[27] Theoretical research has been performed on the singlet state of propadienylidene.[28–35] For example, Klopper's group determined harmonic and anharmonic zero-point vibrational energy (ZPVE) at the CCSD (T) level of theory for the singlet propadienylidene.[32] Wu et al. performed anharmonic vibrational analyses on the electronic ground state of propadienylidene employing vibrational second-order perturbation (VPT2) theory.[33] Additionally, radio-astronomical lines of propadienylidene were observed in 2 famous astronomical sources (TMC-1 and IRC +10216) by means of the IRAM 30 m telescope.[36]

Despite the high reactivity of C_3H_2 carbenes and the importance of addition reactions involving carbenes, the reactions between C_3H_2 carbenes and carbon–nitrogen double bond compounds have not been systematically investigated extensively. The simplest example is $H_2C = NH$, a type of molecule with a $C = N$ double bond, known as methyleneimine, methanimine, and formaldimine. Neutral $H_2C = NH$ is a reactive intermediate that can be produced by pyrolysis of amines and azides.[37–39] $H_2C = NH$ has been observed in interstellar dust clouds.[40] Its gas-phase structure was determined by microwave spectroscopy, and its infrared spectrum and electronic spectrum have also been observed.[41–45]

In the absence of experimental information, theoretical investigations on the above reaction appear to be highly desirable and practicable. Moreover, it has been reported that propadienylidene is the final product of photolysis of cyclopropenylidene.[10] Therefore, in the present study, we systematically investigated the reaction mechanism between propadienylidene and methyleneimine employing the second-order Møller–Plesset perturbation theory (MP2) method so as to reveal the propadienylidene reactivity with unsaturated $C = N$ compounds. In addition reactions between propadienylidene and methyleneimine, 3 different products characterized by 3- or 4-membered rings were obtained via 3 different reaction pathways. The corresponding reaction mechanisms were clarified in detail as well. Hopefully, the present results not only can promote the progress of the relevant experiments, but also can provide insights into the reactivity of C_3H_2 carbene with unsaturated compounds containing $C = N$ double bonds, and enrich the available data on relevant carbene chemistry.

2. Calculation method

The second-order MP2 method[46] in combination with the 6 – 31 + G * basis set was employed to locate all the stationary points along the reaction pathways. Frequency analyses were carried out to confirm the nature of

the minima and transition states. Moreover, intrinsic reaction coordinate (IRC) calculations were 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, were corrected with the zero-point vibrational energy (ZPVE) corrections.

To further refine the calculated energy parameters, single point energy calculations were performed at the CCSD (T) / 6 – 31 + G * level of theory based on the stationary points optimized at the MP2 / 6 – 31 + G * level of theory. As summarized in the Table, both levels can give consistent results for the calculated reaction profile of the addition reaction. For the sake of simplicity, the energetic results at the CCSD (T) / 6 – 31 + G * // MP2 / 6 – 31 + G * level are mainly discussed below if not noted otherwise.

All the calculations were performed using the program Gaussian 98.[47]

Table. The calculated relative energy (in kJ/mol) with respect to the isolated reactants at the MP2 / 6 – 31 + G * level of theory.[a]

Pathways	Relative energies			
Pathway (1)	TS	INT	TS1A	INT1A
	5.6/12.3	–241.6/–204.2	72.2/96.1	–16.3/10.5
	TS1B	P1		
	118.6/142.1	–228.5/–236.5		
Pathway (2R)	TS2AR	INT2AR	TS2BR	P2R
	–31.9/9.3	–66.0/–49.8	–37.8/–12.0	–331.7/–292.9
Pathway (2L)	TS2AL	INT2AL	TS2BL	P2L
	–34.5/7.7	–215.4/–190.5	–23.4/5.0	–370.2/–333.6

[a] The data after the slash refer to the results at the CCSD (T) // MP2 / 6 – 31 + G * level of theory with considering the ZPVE corrections.

3. Results and discussion

Figure 1 shows the 3 possible reaction pathways involving 3 products proposed for the addition reaction between propadienylidene and methyleneimine. Correspondingly, the calculated relative energies for the available stationary points are summarized in the Table.

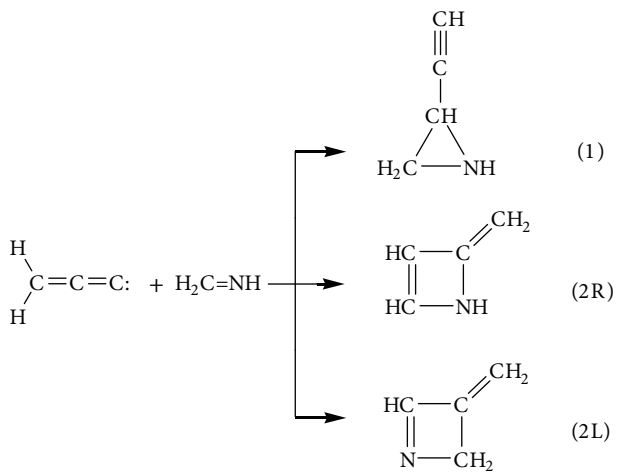

Figure 1. The proposed reaction pathways for the addition reaction between propadienylidene and methyleneimine.

3.1. Reaction pathway (1): the formation of a 3-membered ring product (P1)

The geometric parameters for the reactants (propadienylidene and methyleneimine), transition states (TS, TS1A, and TS1B), intermediates (INT, INT1A), and product (P1) involved in the reaction pathway (1) are displayed in Figure 2. Here, a 3-membered ring product, P1, was obtained in the pathway.

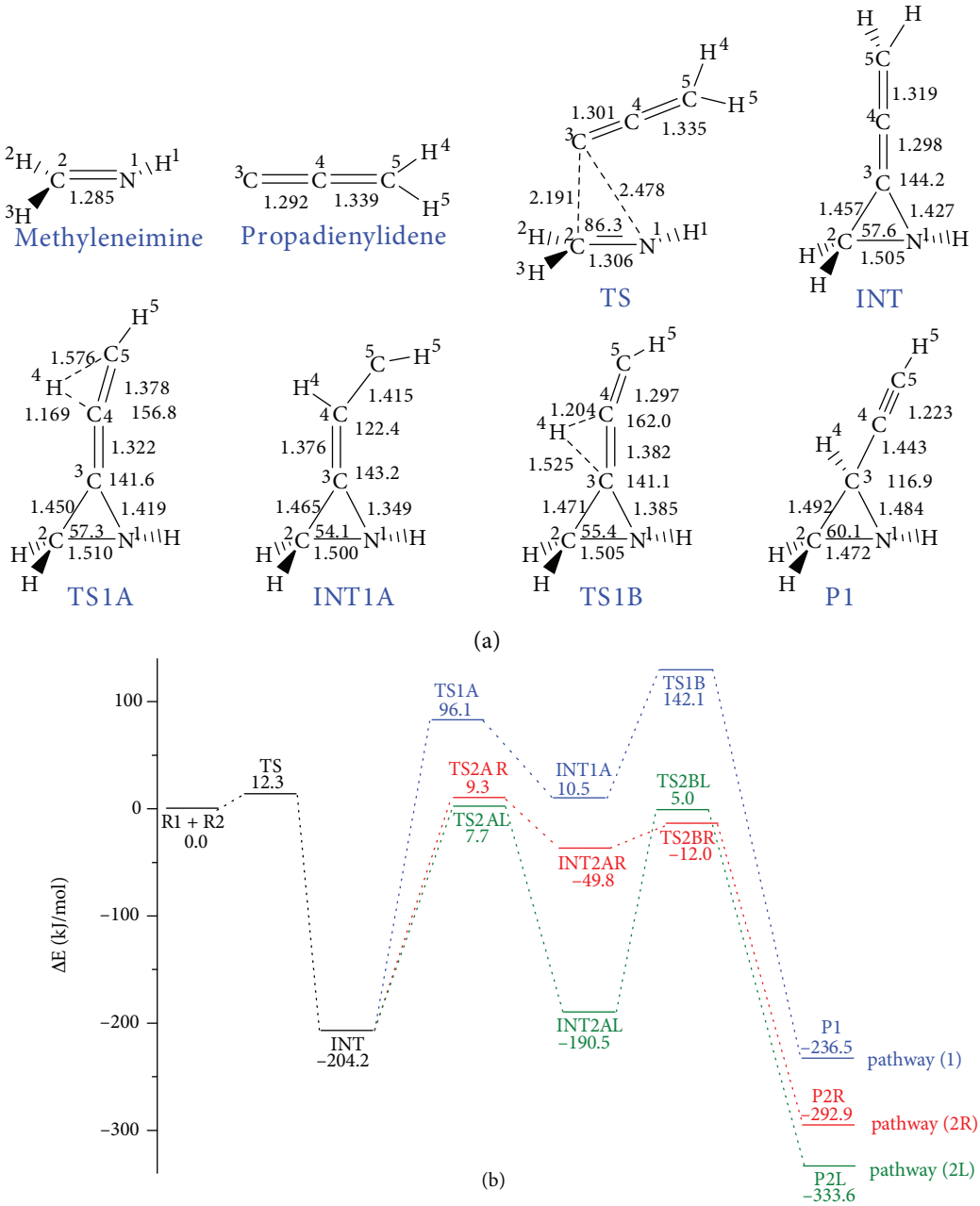

Figure 2. (a): Optimized structures of reactants (propadienylidene and methyleneimine), transition states, intermediates, and products in the reaction pathway (1) at the MP2 / 6 − 31 + G * level of theory, where the bond length and bond angle are in angstroms and degrees, respectively. (b): Reaction profile of addition reaction pathways (1), (2R), and (2L) at the CCSD (T) // MP2 / 6 − 31 + G * level of theory.

The first initial intermediate, INT, was formed in the pathways (1), (2R), and (2L) via a rather low barrier of 12.3 kJ/mol. As shown in Figure 2, the distances from C^3 to N^1 and C^2 in TS are 2.478 and 2.191 Å, respectively. Compared with the reactants, the bond lengths of C^3C^4, C^4C^5, and O^1C^2 are only slightly changed (1.301 vs. 1.292, 1.335 vs. 1.339, and 1.306 vs. 1.285 Å). The smoothness of the full IRC shown in Figure 3 further indicates that TS connects reactants with the 3-membered ring intermediate INT.

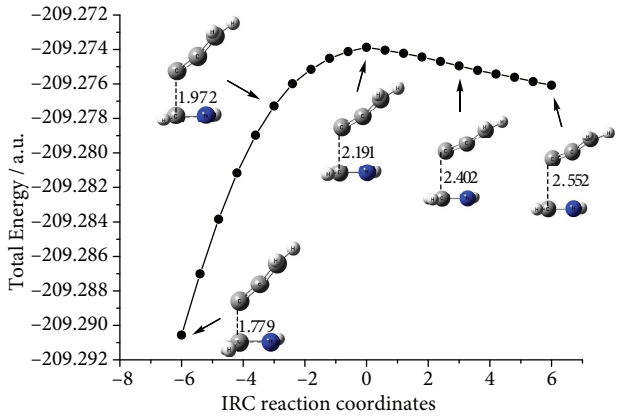

Figure 3. IRC of TS and geometry evolution.

As displayed in Figure 2, the C^4 of INT adopts *sp* hybridization and its 2 C - C bond lengths are 1.319 (C^4 - C^5) and 1.298 (C^3 - C^4) Å, respectively, which are both between the general C = C double bond (about 1.33 Å) and C ≡ C triple bond (about 1.20 Å). These bond lengths suggest that INT possesses the feature of a normal allene, which can be further isomerized into an alkyne structure. Consequently, the hydrogen atom of INT is transferred from the C^5 to C^4 atom via TS1A in the second step of pathway (1), resulting in the formation of an intermediate INT1A.

The C^4 of INT1A adopts sp^2 hybridization and its C^4 - C^5 and C^3 - C^4 bonds are changed into a single and a double bond, respectively. As for the C^5 atom, it has a pair of lone electrons, making the INT1A exhibit a feature of carbenes. In other words, INT1A is unstable and can be rearranged into a more stable structure.

By shifting the H^4 atom from the C^4 to adjacent C^3, INT1A is converted to P1 via TS1B. Here, P1 is the most stable structure in pathway (1). Obviously, the C^3 of P1 is sp^3 hybridization and both the C^4 and C^5 are *sp* hybridization. Therefore, the bond between the C^4 and C^5 is a triple bond (1.223 Å), whose length is rather shorter than that of the bond between C^3 and C^4 (1.443 Å).

The barrier heights of the 3 steps in pathway (1) are 12.3, 300.3, and 131.6 kJ/mol, respectively. Therefore, the second step is the rate-determining step along pathway (1).

3.2. Reaction pathways (2R) and (2L): the formation of a 4-membered ring product (P2R and P2L)

The geometric parameters of the transition states, intermediate, and product involved in the reaction pathways (2R) and (2L) are displayed in Figure 4. The corresponding reaction profiles are illustrated in Figure 2.

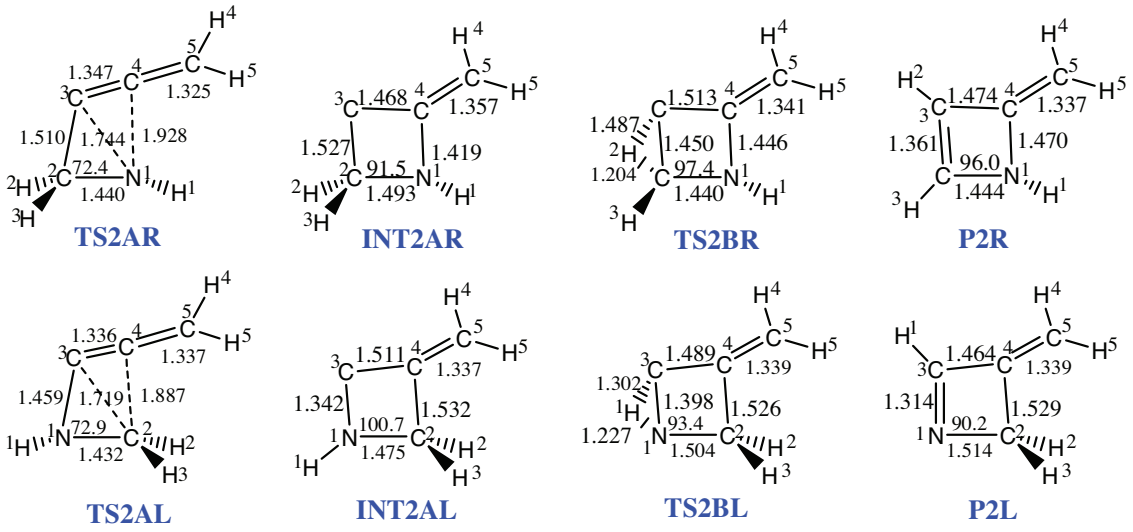

Figure 4. Optimized structures of transition states, intermediate, and products in the reaction pathways (2R) and (2L) at the MP2 / 6 – 31 + G * level of theory, where the bond length and bond angle are in angstroms and degrees, respectively.

Similar to the reaction pathway (1), a common intermediate (INT) is formed firstly in the pathways (2R) and (2L). Due to the existence of tension in the 3-membered ring, the N^1 - C^3 bond opens to form an intermediate INT2AR via TS2AR in the second step of the pathway (2R), where the barrier height is 213.5 kJ/mol. Similarly, the C^2 - C^3 bond in INT opens to form an intermediate INT2AL via TS2AL in the second step of the pathway (2L), where the barrier height is 211.1 kJ/mol.

Both INT2AR and INT2AL possess the characters of carbene, where both the C^3 atoms have a pair of lone electrons. The third step of the pathway (2R) is that one H atom on the C^2 of INT2AR is transferred to the C^3 to form a more stable structure P2R via TS2BR, where the barrier height is 37.8 kJ/mol. Based on the analysis of the imaginary frequency and the calculation of the IRC, it can be proved that TS2BR actually connects INT2AR with P2R. With regard to the third step of the pathway (2L), it is the H atom on the N^1 of INT2AL that is transferred to the C^3 to form a more stable structure P2L via TS2BL. The corresponding barrier height is 195.5 kJ/mol, which is much higher than that of the INT2AR $\rightarrow$ P2R progress.

As for the structure of P2R, the bond lengths of C^2 - C^3 and C^4 - C^5 are 1.361 and 1.337 Å, respectively, which are slightly longer than that of a general C = C double bond. At the same time, the bond length of C^3 - C^4 of P2R is 1.474 Å, which is approximated to that of a general C - C single bond. Moreover, further energy analyses suggest that the energy of P2R is lower than that of the reactants by about 292.9 kJ/mol. From the calculated bond length and the stability, one can say that P2R is a stable conjugated diene and it is the ultimate product of the pathway (2R). As for the P2L, its energy is lower than that of the reactants by about 333.6 kJ/mol, and it is the ultimate product of the pathway (2L).

3.3. Comparisons of the 3 reaction pathways

As mentioned above, 3- and 4-membered ring products can be produced between propadienylidene and methyleneimine through 3 different reaction pathways. The barrier heights of the rate-determining step in

reaction pathway (1), (2R), and (2L) are 300.3, 213.5, and 211.1 kJ/mol, respectively. The reaction pathway (2L) with the lowest barrier height should be the most favorable channel from the kinetic viewpoint. On the other hand, the corresponding 3 products P1, P2R, and P2L are all stable because their energies are all lower than their corresponding reactants by 236.5, 292.9, and 333.6 kJ/mol, respectively. Furthermore, the most favorable product P2L has also been confirmed, suggesting that the reaction pathway (2L) is also a favorable channel from the thermodynamical viewpoint.

To better understand the reaction activities of the 3 pathways mentioned above, we investigated the relevant molecular orbitals for the INT, TS1A, and TS2AR. As displayed in Figure 5, the formations of the transition states TS1A and TS2AR in pathways (1) and (2R) are associated with the third occupied molecular orbital (HOMO - 3) below the highest occupied molecular orbital (HOMO). For the TS2AR, the nonbonding p orbital of N1 atom can be overlapped with the π orbital formed by the C3, C4, and C5 atoms. As a result, the lone pair of electrons of the N1 atom can be shifted to the π orbital, resulting in an energy decrease of the formed orbital. Similarly, the same is also true for the transition state TS2AL in pathway (2L). On the other hand, the corresponding electron shift cannot occur for the TS1A since there is no orbital overlap between the shifting H atom and the π orbital mentioned above. Moreover, the high tension of the formed 3-membered ring associated with the shifting H atom is unfavorable in energy relative to that of the 4-membered ring in the TS2AR. Therefore, it is easy to form the TS2AR and TS2AL relative to TS1A. In other words, the corresponding energy barriers required to overcome in the pathways (2R) and (2L) should be lower than that of the pathway (1). Actually, as also shown in Figure 5, this point can be further reflected by the lower orbital energy of TS2AR relative to that of TS1A.

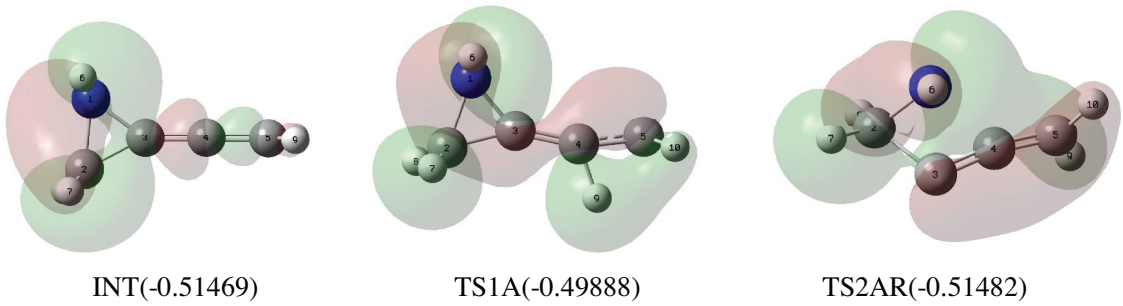

Figure 5. The calculated HOMO - 3 orbitals for INT, TS1A, and TS2AR (from left to right), where the data in parentheses refer to the corresponding orbital energies (in a.u.).

4. Conclusions

In this study, the addition reaction mechanism between propadienylidene and methyleneimine was systematically investigated employing the MP2 / 6 – 31 + G * and CCSD (T) / 6 – 31 + G * levels of theory. In 3 pathways, it was found that one initial intermediate characterized by the 3-membered ring formed firstly. Then 3 different products characterized by 3- or 4-membered rings were obtained through different pathways. The barrier heights of the rate-determining step of the 3 reaction pathways are 300.3, 213.5, and 211.1 kJ/mol, respectively. The reaction pathway (2L) is the most favorable reaction kinetically. On the other hand, the corresponding 3 products P1, P2R, and P2L are all stable because their energies are lower than their corresponding reactants by 236.5, 292.9, and 333.6 kJ/mol, respectively. P2L is the most stable product among them, which suggests that the pathway (2L) should also be a favorable process thermodynamically.

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