



Ab initio study of mechanism of forming germanic bis-heterocyclic compound between germylene carbene ($\text{H}_2\text{Ge}=\text{C}:$) and acetone

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ABSTRACT

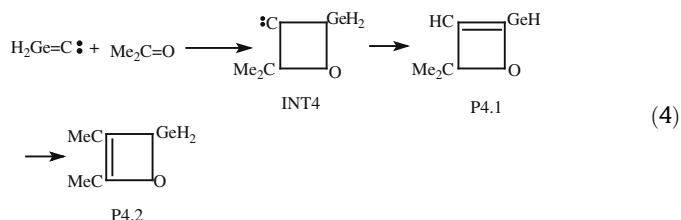
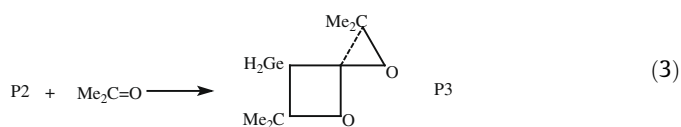
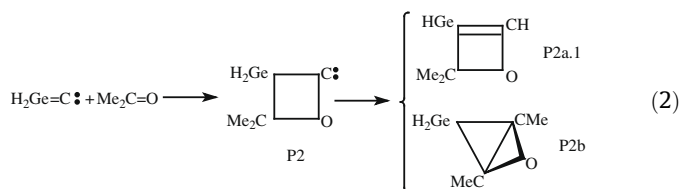
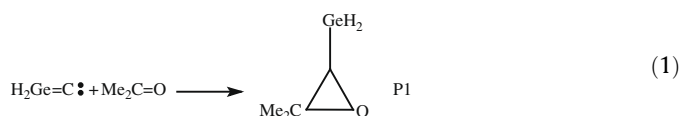
The mechanism of the cycloaddition reaction of forming germanic bis-heterocyclic compound between singlet germylene carbene and acetone has been investigated with MP2/6-31G* method, including geometry optimization and vibrational analysis for the involved stationary points on the potential energy surface. The energies of the different conformations are calculated by CCSD (T)/MP2/6-31G* method. From the potential energy profile, it can be predicted that the dominant reaction pathway of the cycloaddition reaction of forming germanic bis-heterocyclic compound consists of three steps: (1) the two reactants firstly form an intermediate INT4 through a barrier-free exothermic reaction of 181.4 kJ/mol; (2) INT4 further reacts with acetone (R2) to form an intermediate (INT5), which is also a barrier-free exothermic reaction of 148.9 kJ/mol; (3) INT5 then isomerizes to a germanic bis-heterocyclic product P5 via a transition state TS5 with an energy barrier of 53.3 kJ/mol.

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1. Introduction

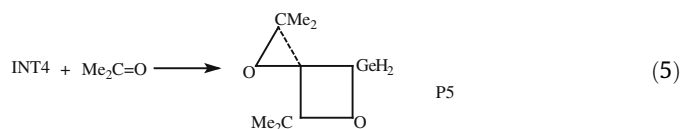
Since unsaturated carbene was recognized as an active intermediate in 1960s, it has not only attracted much attention from theoretical chemists but also has been practically applied to organic chemistry [1,2]. For example, it has been proved that unsaturated carbene can provide a simple and direct way for synthesizing the small-ring, highly strained compounds as well as those that can hardly be synthesized through conventional ways [2]. So far, much theoretical study has been done on the rearrangement reaction [3,4] and the insertion reaction [5,6] of alkylidene carbene [$\text{R}_1, \text{R}_2\text{C}=\text{C}:$ ($\text{R}_1, \text{R}_2 = \text{H}, \text{Me}, \text{F}, \text{Cl}, \text{Br}, \text{Ph}, \text{Ar}$)]. Apeloig and Fox [7,8] have made experimental and theoretical studies on the three-dimensional selectivity of substituting groups from the products of the vinylidene-olefins addition. And we have done systemic studies on the cycloaddition reaction of alkylidene carbene [9–13]. However, studies of unsaturated carbene have so far been limited to alkylidene carbene and its reactions and there has been no published report of studies of germylene carbene ($\text{H}_2\text{Ge}=\text{C}:$) and its derivatives. It is a new branch of unsaturated carbene chemistry. It is quite difficult to investigate mechanism of cycloaddition reaction directly by experimental methods due to the high activity of germylene carbene; therefore, the theoretical study is more practical. To explore the rules of cycloaddition reaction between germylene carbene and the asymmetric π -bonded compounds, germylene carbene and acetone were selected as model molecules. The cycloaddition reaction mechanism was investigated and analyzed theo-

retically. The results show that this reaction proceeds in the following five possible pathways (considering the hydrogen transfer and methyl transfer):



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2. Calculation methods

MP2/6-31G* [14] implemented in the GAUSSIAN98 package is employed to locate all the stationary points along the reaction pathways. Full optimization and vibrational analysis are done for the stationary points on the reaction profile. Zero-point energy and CCSD(T) corrections are included for the energy calculations. In order to further confirm the correctness of the relevant species, vibration analysis are included, and the intrinsic reaction coordinate (IRC) [15,16] was also calculated for all the transition states appearing on the potential energy profile.

3. Results and discussion

3.1. Reaction (1): channels of forming three-membered ring product P1

The geometrical parameters for the intermediate (INT1), transition state (TS1) and product (P1) appearing in reaction (1) between germylene carbene and acetone are given in Fig. 1. The energies are listed in Table 1, and the potential energy surfaces for the cycloaddition reaction are shown in Fig. 2. The unique imaginary frequency of the transition state TS1 through vibrational analysis is 117.4i, therefore, this transition state can be affirmed as the real one. IRC (with the step-length of 0.1 amu^{-1/2}bohr) analysis of TS1 confirms that TS1 connects INT1 and P1. According to Fig. 2, it can be intuitively seen that reaction (1) is composed of two steps: the first one is that the two reactants (R1, R2) firstly form an intermediate INT1, which is a barrier-free exothermic reaction with ΔE of 105.8 kJ/mol; and the second one is an isomerization of interme-

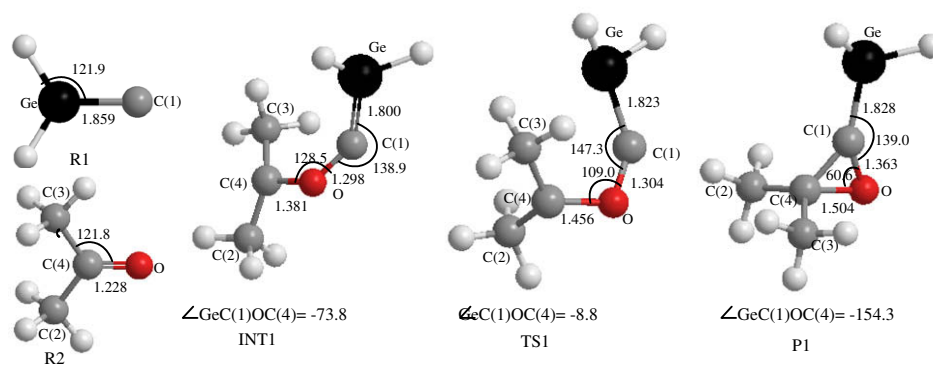


Fig. 1. Optimized MP2/6-31G* geometrical parameters and the atomic numbering for the species in cycloaddition reaction (1). Bond lengths (Å) and angles (°).

Table 1

Zero point energy (ZPE, a.u), total energies (E_T , a.u) and relative energies (E_R , kJ/mol) for the species from various theoretical methods.

Reaction	Species	ZPE	MP2/6-31G*		CCSD (T)/MP2/6-31G*	
			^a E_T	^b E_R	^a E_T	^b E_R
Reaction (1)	R1 + R2	0.10044	-2304.65643	0.0	-2304.75918	0.0
	INT1	0.10662	-2304.71958	-165.8	-2304.79947	-105.8
	TS1(INT1 – P1)	0.10655	-2304.69633	-104.8	-2304.78210	-60.2
	P1	0.10775	-2304.79756	-370.5	-2304.88126	-320.5
Reaction (2)	R1 + R2	0.10044	-2304.65643	0.0	-2304.75918	0.0
	TS2(INT1 – P2)	0.10527	-2304.69577	-103.3	-2304.78417	-65.6
	P2	0.10658	-2304.75246	-252.1	-2304.84427	-223.4
	TS2a(P2 – P2a)	0.10455	-2304.71086	-142.9	-2304.80134	-110.7
	P2a	0.10777	-2304.72918	-191.0	-2304.82456	-171.7
	TS2a.1(P2a – P2a.1)	0.10564	-2304.70978	-140.1	-2304.79897	-104.5
	P2a.1	0.11172	-2304.80244	-383.4	-2304.88897	-340.8
	TS2b(P2 – P2b)	0.10430	-2304.65632	0.3	-2304.74136	46.8
	P2b	0.10760	-2304.79089	-353.0	-2304.86989	-290.7
Reaction (3)	P2 + R2	0.19250	-2497.38294	0.0	-2497.33645	0.0
	INT3	0.19782	-2497.21304	446.1	-2497.33951	-8.0
	TS3(INT3 – P3)	0.19738	-2497.20175	475.7	-2497.33062	15.3
	P3	0.19862	-2497.28765	250.2	-2497.41943	-217.9
Reaction (4)	R1 + R2	0.10044	-2304.65643	0.0	-2304.75918	0.0
	INT4	0.10725	-2304.74368	-229.1	-2304.82829	-181.4
	TS4.1(INT4 – P4.1)	0.10631	-2304.72852	-189.3	-2304.82034	-160.6
	P4.1	0.11158	-2304.83238	-462.0	-2304.91022	-396.6
	TS4.2(P4.1 – P4.2)	0.10592	-2304.72336	-175.7	-2304.81238	-139.7
	P4.2	0.10895	-2304.87397	-571.2	-2304.95294	-508.7
Reaction (5)	INT4 + R2	0.19318	-2497.18166	0.0	-2497.32047	0.0
	INT5	0.19869	-2497.25433	-190.8	-2497.37718	-148.9
	TS5(INT5 – P5)	0.19721	-2497.22848	-122.9	-2497.35686	-95.6
	P5	0.19972	-2497.31759	-356.9	-2497.44624	-330.2

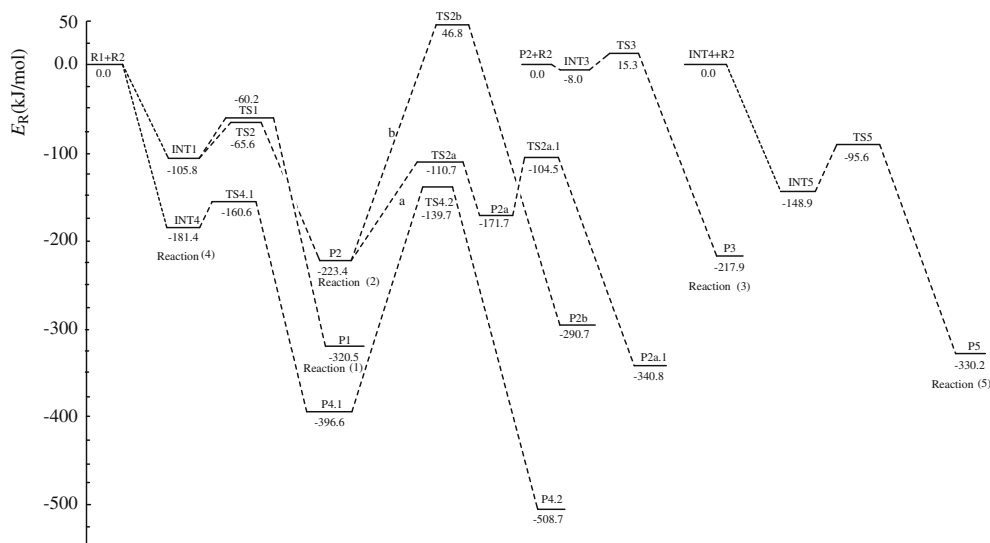


Fig. 2. The potential energy surface for the cycloaddition reactions between germylene carbene and acetone with CCSD (T)//MP2/6-31G*.

diate INT1 to a three-membered ring product P1 via a transition state TS1, with an energy barrier of 45.6 kJ/mol.

3.2. Reaction (2): channels of forming four-membered ring product P2, H-transfer products (P2a, P2a.1) and CH₃-transfer product P2b

The geometrical parameters for the transition states (TS2, TS2a, TS2a.1, TS2b) and products (P2, P2a, P2a.1, P2b) appearing in reaction (2) between germylene carbene and acetone are given in Fig. 3. The energies are listed in Table 1, and the potential energy surfaces for the cycloaddition reaction are shown in Fig. 2. The unique imaginary frequencies of the transition states TS2, TS2a, TS2a.1 and TS2b are 151.3i, 576.2i, 436.0i and 685.8i, respectively. Therefore, these transition states can be affirmed as the real ones. Their IRC (with the step-length of 0.1 amu^{-1/2}bohr) analysis con-

firms that TS2 connects INT1 and P2; TS2a connects P2 and P2a, TS2a.1 connects P2a and P2a.1, and TS2b connects P2 and P2b. It can be observed from Fig. 2 that the process of reaction (2) is as following: the first step is a barrier-free exothermic reaction of 105.8 kJ/mol, leading to an intermediate INT1, which then isomerizes to a four-membered ring product P2 via a transition state TS2 with a barrier of 40.2 kJ/mol. Subsequently, the product P2 undergoes hydrogen transfer and methyl transfer by path a and b. The H-transfer reaction (a) consists of two steps: the first one is that product P2 isomerizes to H-transfer product P2a via transition state TS2a with energy barrier of 112.7 kJ/mol; and the second one is an isomerization of P2a to H-transfer product P2a.1 via a transition state TS2a.1, with an energy barrier of 67.2 kJ/mol. Because of such a high barrier and a higher energy of P2a than P2 by 51.7 kJ/mol, the reaction P2 → P2a is forbidden in thermody-

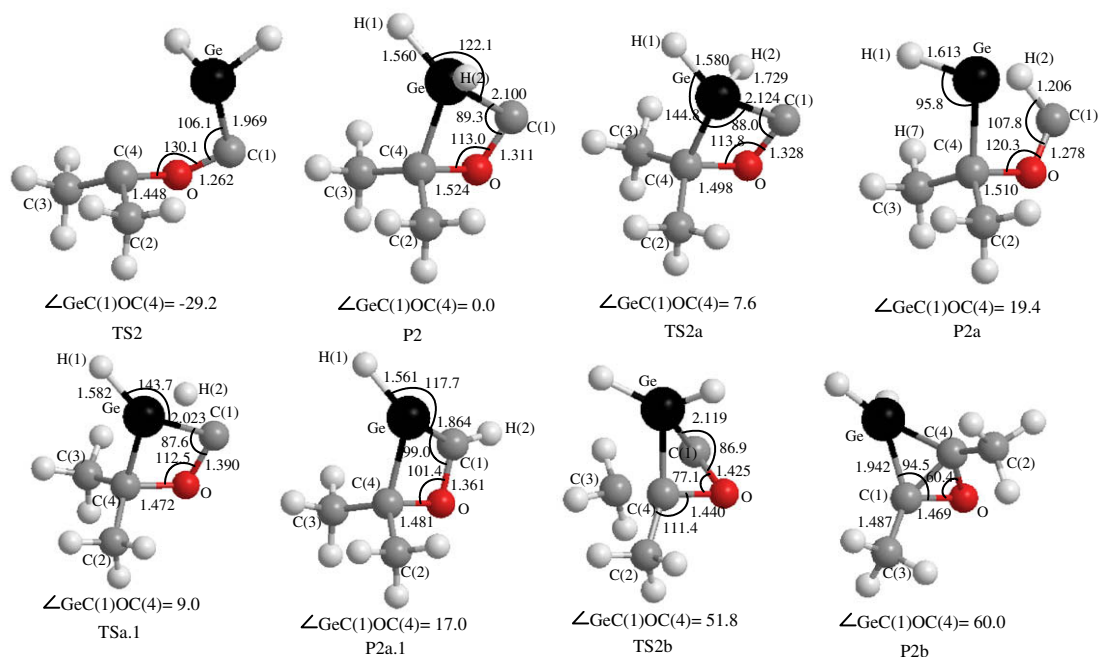


Fig. 3. Optimized MP2/6-31G* geometrical parameters of TS2, P2, TS2a, P2a, TS2a.1, P2a.1, TS2b, P2b and the atomic numbering for cycloaddition reaction (2). Bond lengths (Å) and angles (°).

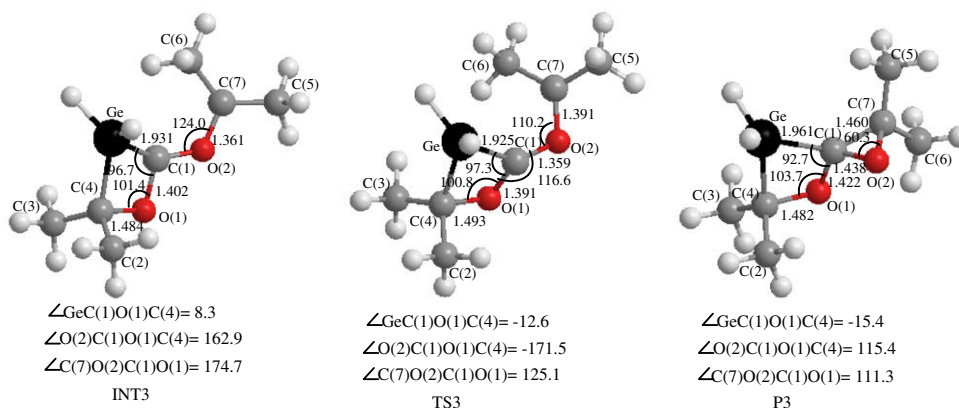


Fig. 4. Optimized MP2/6-31G* geometrical parameters of INT3, TS3, P3 and the atomic numbering for cycloaddition reaction (3). Bond lengths (Å) and angles (°).

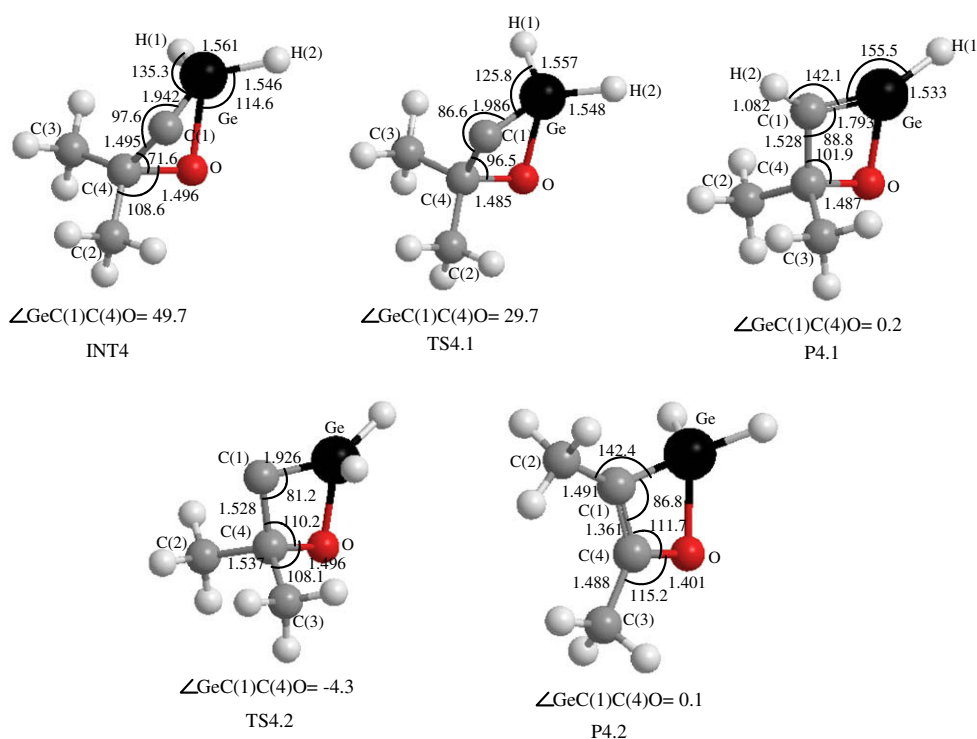


Fig. 5. Optimized MP2/6-31G* geometrical parameters of INT4, TS4.1, P4.1, TS4.2, P4.2 and the atomic numbering for cycloaddition reaction (4). Bond lengths (Å) and angles (°).

namics, this reaction will end in P2. The CH₃-transfer reaction (B) is composed of only one step, that is, P2 undergoes methyl transfer via a transition state TS2b with an energy barrier of 270.2 kJ/mol, resulting in the formation of P2b. Due to the high barrier, path b will also end in P2 under normal circumstances. According to the comparison of reaction (2) with reaction (1), the energy of TS1 is 5.4 kJ/mol higher than that of TS2, so reaction (2) will be the dominant reaction channel.

3.3. Reaction (3): channels of forming germanic bis-heterocyclic product P3

In reaction (3), the active four-membered ring product P2 further reacts with acetone (R2) to form the germanic bis-heterocyclic compound P3. The geometric parameters for the intermediate INT3, the transition state TS3 and the product P3 appearing in reaction (3) are given in Fig. 4. The energies are listed in Table 1. The potential energy surface for reaction (3) is illustrated in Fig. 2. The unique imaginary frequency of the transition state TS3 is

89.8i, and therefore the transition state can be affirmed as the real one. IRC (with the step-length of 0.1 amu^{-1/2}bohr) analysis confirms that TS3 connects INT3 and P3. According to Fig. 2, the process of reaction (3) is as following: on the basis of P2 formed from the reaction (2) between R1 and R2, P2 further reacts with acetone (R2) to form an intermediate INT3 through a barrier-free exothermic reaction of 8.0 kJ/mol. Then, INT3 isomerizes to a germanic bis-heterocyclic product P3 via a transition state TS3, for which the energy barrier is 23.3 kJ/mol.

3.4. Reaction (4): channels of forming four-membered ring intermediate INT4, H-transfer product P4.1 and CH₃-transfer product P4.2

The geometrical parameters for the intermediate INT4, the transition states (TS4.1, TS4.2) and products (P4.1, P4.2) appearing in reaction (4) between germylene carbene and acetone are given in Fig. 5. The energies are listed in Table 1, and the potential energy surfaces for the cycloaddition reaction are shown in Fig. 2. The un-

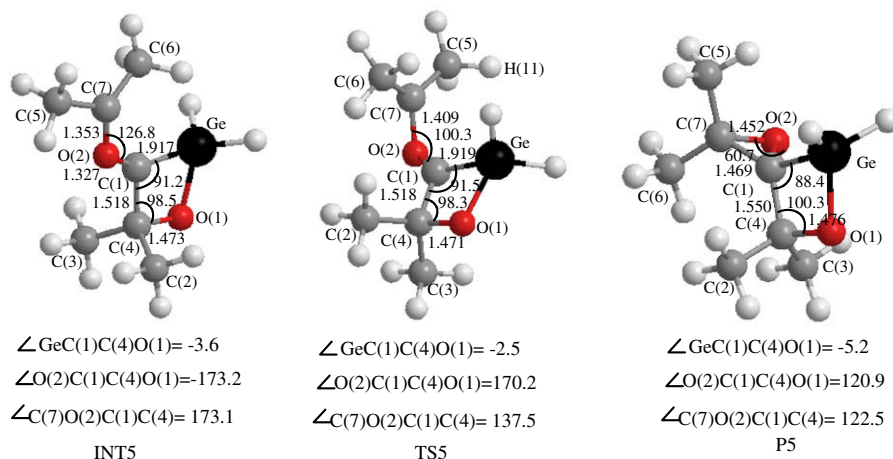


Fig. 6. Optimized MP2/6-31G* geometrical parameters of INT5, TS5, P5 and the atomic numbering for cycloaddition reaction (5). Bond lengths (Å) and angles (°).

ique imaginary frequencies of the transition states TS4.1 and TS4.2 are 389.1i and 689.5i, therefore, these transition states can be affirmed as the real ones. Their IRC (with the step-length of $0.1 \text{ amu}^{-1/2} \text{ bohr}$) analysis confirms that TS4.1 connects INT4 and P4.1, TS4.2 connects P4.1 and P4.2. It can be observed from Fig. 2 that reaction (4) consists of three steps. The first one is a barrier-free exothermic reaction of 181.4 kJ/mol, leading to a twist four-membered ring intermediate INT4, which then isomerizes to a four-membered planar ring H-transfer product P4.1 via a transition state TS4.1, with an energy barrier of 20.8 kJ/mol. Finally the product P4.1 isomerizes to CH₃-transfer product P4.2 via transition state TS4.2, with barrier of 256.9 kJ/mol. According to the comparison of reaction (4) with reaction (3), the energy of TS2 is 19.4 kJ/mol higher than that of TS4.1, so reaction (4) will be the dominant reaction channel.

3.5. Reaction (5): channels of forming germanic bis-heterocyclic product P5

In reaction (5), the active four-membered ring intermediate INT4 further reacts with acetone (R2) to form the germanic bis-heterocyclic product P5. The geometric parameters for the intermediate INT5, the transition state TS5 and the product P5 appearing in reaction (5) are given in Fig. 6. The energies are listed in Table 1. And the potential energy surface for reaction (5) is illustrated in Fig. 2. The unique imaginary frequency of the transition state TS5 is 171.8i, and the transition state can therefore be affirmed as the real one. IRC (with the step-length of $0.1 \text{ amu}^{-1/2} \text{ bohr}$) analysis of TS5 confirms that TS5 connects INT5 and P5. According to Fig. 2,

the process of reaction (5) is as following: on the basis of INT4 created from the reaction (4) between R1 and R2, INT4 further reacts with acetone (R2) to form the intermediate INT5 through a barrier-free exothermic reaction of 148.9 kJ/mol. Then, INT5 isomerizes to a germanic bis-heterocyclic product P5 via a transition state TS5, for which the barrier is 53.3 kJ/mol. Compared reaction (5) with reaction (4), it is realizing that the two reaction form a mutual competition reaction due to scrambling for INT4 together. In reaction (4), INT4 isomerizes to P4.1 with an energy barrier of 20.8 kJ/mol; However, in reaction (5), INT4 and R2 form an intermediate INT5 just through a barrier-free exothermic reaction of 148.9 kJ/mol. Compared reaction (5) with reaction (4), it can be known that reaction (5) will be the dominant reaction channel.

3.6. Theoretical analysis and explanation of the dominant reaction channel

According to the above analysis, reaction (5) should be the dominant reaction channel of the cycloaddition reaction between singlet germylene carbene and acetone namely:



The mechanism of reaction (5) could be explained with the molecular orbital diagram (Figs. 7 and 8) and Figs. 5 and 6. According to Figs. 5 and 7, as germylene carbene (R1) initially interacts with acetone (R2), the [2 + 2] cycloaddition of the bonding π -orbitals firstly results in a twist four-membered ring intermediate INT4.

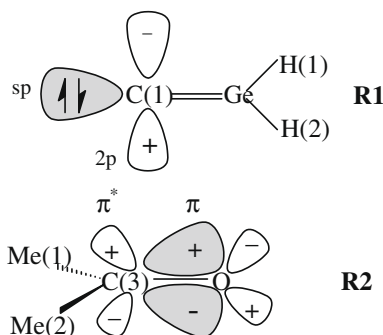


Fig. 7. A schematic interaction diagram for the frontier orbitals of $\text{H}_2\text{Ge}=\text{C}$ (R1) and $\text{Me}_2\text{C}=\text{O}$ (R2).

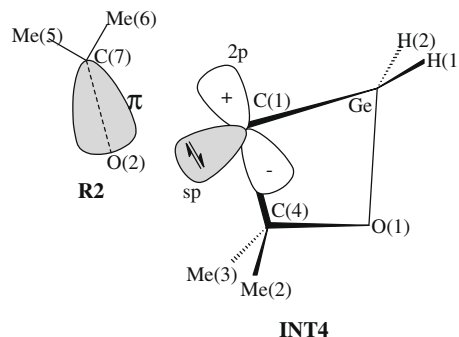


Fig. 8. A schematic interaction diagram for the frontier orbitals of INT4 and $\text{Me}_2\text{C}=\text{O}$ (R2).

the conformation of INT4, atom C(1) is unsaturated. So, INT4 may further reacts with acetone (R2) to form the germanic bis-heterocyclic product P5. The mechanism of this reaction could be explained with the molecular orbital diagram (Figs. 6 and 8). When INT4 initially interacts with acetone (R2), C(1) in INT4 will be hybridized into sp^2 hybrid orbital and reacts with acetone to form an intermediate INT5. As the reaction goes on, the dihedral angles $\angle O(2)C(1)C(4)O(1)$ (INT5:186.8°, TS5:170.2°, P5:120.9°) and $\angle C(7)O(2)C(1)O(2)$ bond (INT5:1.353 Å, TS5:1.409 Å, P5:1.452 Å) gradually lengthens. These changes finally make the C(1) in INT5 hybridize to sp^3 hybrid orbital after the transition state TS5, forming the more stable germanic bis-heterocyclic product P5.

4. Conclusion

On the basis of the potential energy surface obtained with the CCSD (T)//MP2/6-31G* method for the cycloaddition reaction between singlet germylene carbene and acetone, it can be predicted that the dominant reaction pathway of the cycloaddition reaction of forming germanic bis-heterocyclic compound is reaction (5). The process of this reaction is as following: (1) the two reactants firstly form an intermediate INT4 through a barrier-free exothermic reac-

tion of 181.4 kJ/mol; (2) INT4 further reacts with acetone (R2) to form an intermediate INT5, which is also a barrier-free exothermic reaction of 148.9 kJ/mol; (3) INT5 then isomerizes to a germanic bis-heterocyclic product P5 via a transition state TS5 with an energy barrier of 53.3 kJ/mol.

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