

ORIGINAL ARTICLE

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa





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from Me₂Si=Si: and acetaldehyde

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Density functional theory study of mechanism

of forming a spiro-Si-heterocyclic ring compound

Received 18 June 2014; accepted 6 February 2015 Available online 14 February 2015

KEYWORDS

Me₂Si—Si; Four-membered Si-heterocyclic ring silylene; Spiro-Si-heterocyclic ring compound; Potential energy profile **Abstract** The H₂Si=Si: and its derivatives (X₂Si=Si:, X = H, Me, F, Cl, Br, Ph, Ar...) is a new species. Its cycloaddition reaction is a new area for the study of silylene chemistry. The mechanism of the cycloaddition reaction between singlet Me₂Si=Si: and acetaldehyde has been investigated with the B3LYP/6-31G^{*} method in article. From the potential energy profile, it could be predicted that the reaction has one dominant reaction pathway. The reaction rule presented is that the two reactants firstly form a four-membered Si-heterocyclic ring silylene through the [2 + 2] cycloaddition reaction. Because of the 3p unoccupied orbital of Si: atom in the four-membered Si-heterocyclic ring silylene and the π orbital of acetaldehyde forming a $\pi \rightarrow p$ donor-acceptor bond, the four-membered Si-heterocyclic ring silylene further combines with acetaldehyde to form an intermediate. Because the Si atom in intermediate happens sp³ hybridization after transition state, then, intermediate isomerizes to a spiro-Si-heterocyclic ring Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Since unsaturated carbene [X₂C=C: (X = H, Me, F, Cl, Br, Ph, Ar...)] was recognized as an active intermediate in the 1960s, it has not only attracted much attention from theoretical chemists, but also has been practically applied to the organic chemistry (Stang, 1982, 1978). For example, it

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Peer review under responsibility of King Saud University.



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 (Stang, 1978). So far, in depth exploration has been done on the rearrangement reaction of alkylidene carbene (Krishnan et al., 1981; Frisch et al., 1981), and the insertion reaction of alkylidene carbene has also been studied (Wardrop and Zhang, 2002; Feldman and Perkins, 2001). Apeloig and Fox have made experimental and theoretical studies on the 3-dimensional selectivity of substituting groups from the products of the vinylidene-olefin addition reaction of alkylidene carbene (Apeloig et al., 1983; Fox et al., 1986). Meanwhile, we have done a relatively systematic theoretical study on the cycloaddition reaction of alkylidene carbene (Lu and Wang, 2003, 2004; Lu et al., 2005, 2007, 2008).

http://dx.doi.org/10.1016/j.arabjc.2015.02.001

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However, studies of unsaturated ethylenic compounds of the four main group elements have been limited to vinylidene and its reactions so far. There have been no published reports about analog X_2 Si=Si: (X = H, Me, F, Cl, Br, Ph, Ar...) of unsaturated carbene, and they are new study field of unsaturated silvlene chemistry. It is quite difficult to investigate the mechanisms of the cycloaddition reaction by experimental methods directly, due to the high activity of unsaturated silylene; therefore, the theoretical study is more practical. To explore the rules of the cycloaddition reactions between unsaturated silylene [X₂Si=Si: (X = H, Me, F, Cl, Br, Ph, Ar...)] and the asymmetric π -bonded compounds, Me₂Si=Si: and acetaldehyde were selected as the model molecules, and its mechanisms were investigated and analyzed theoretically. The results show that there are four possible pathways of the cycloaddition reaction (considering the H and Me transfer simultaneously) as follows:







The research result indicates the laws of cycloaddition reaction between Me₂Si=Si: and acetaldehyde, and laid the theory foundation of the cycloaddition reaction between H₂Si=Si: and its derivatives (X₂Si=Si:, X = H, Me, F, Cl, Br, Ph, Ar...) and asymmetric π -bonded compounds, which are significant for the synthesis of small-ring and spiro-Si-heterocyclic ring compounds. The study extends research area and enriched the research content of silylene chemistry.

2. Calculation method

B3LYP/6-31G^{*} (Lee et al., 1988) implemented in the Gaussian 98 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 is included for the energy calculations. To explicitly establish the relevant species, the intrinsic reaction coordinate (IRC) (Lee 1970; Ishida et al., 1977) is also calculated for all the transition states appearing on the cycloaddition energy surface profile.

3. Results and discussion

3.1. Reaction (1): channels of forming a four-membered Si-heterocyclic ring silylene (P1), methyl transfer products (P1.1, P1.3) and hydrogen transfer products (P1.2)

The geometrical parameters of intermediate (INT1), transition states (TS1, TS1.1, TS1.2, TS1.3) and products (P1, P1.1, P1.2, P1.3) appearing in reaction (1) between Me₂Si=Si: and acetaldehyde are given in Fig. 1. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. According to Fig. 2, it can be seen that reaction (1) consists of five steps: the first step is that the two reactants (R1, R2) form an intermediate (INT1), which is a barrier-free exothermic reaction of 67.7 kJ/mol; the second step is that the intermediate (INT1) isomerizes to a four-membered Si-heterocyclic ring silylene (P1) via the transition state (TS2) with an energy barrier of 24.5 kJ/mol; the third and fourth steps are that the four-membered Si-heterocyclic ring silvlene (P1) undergoes Si-Si and C(3)-Si(2) methyl transfer via the transition states (TS1.1 and TS1.3) with energy barriers of 151.1 and 91.4 kJ/mol, respectively, resulting in the formation of products (P1.1 and P1.3). The fifth step is that the four-membered Si-heterocyclic ring silvlene (P1) undergoes C(3)—Si(2) hydrogen transfer via the transition state (TS1.2) with energy barrier of 144.0 kJ/mol, resulting in the formation of product (P1.2). The reactions of P1 \rightarrow P1.1, P1 \rightarrow P1.2 and $P1 \rightarrow P1.3$ are prohibited in thermodynamics, because the energies of P1.1, P1.2 and P1.3 are 55.5, 50.6 and 58.1 kJ/mol higher than that of P1, and the reaction (1) will be ended in product P1.

3.2. Reaction (2): channel of forming a spiro-Si-heterocyclic ring compound (P2)

In reaction (3), the four-membered Si-heterocyclic ring silylene (P1) further reacts with acetaldehyde to form a spiro-Si-heterocyclic ring compound (P2). The geometrical parameters of intermediate (INT2), transition state (TS2) and product (P2) appearing in reaction (2) are given in Fig. 3. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. According to Fig. 2, it can be seen that the process of the reaction (3) is as follows: on the basis of P1 formed in the reaction (1), the P1 further reacts with acetaldehyde (R2) to form an intermediate (INT2), which is also a barrier-free exothermic reaction of 38.3 kJ/mol; and then the intermediate (INT2) isomerizes to



Figure 1 Optimized B3LYP/6-31G^{*} geometrical parameters and the atomic numbering for the species in cycloaddition reaction (1). Bond lengths and bond angles are in angstrom and degree, respectively.

a spiro-Si-heterocyclic ring compound (P2) via the transition state (TS2) with an energy barrier of 28.0 kJ/mol.

3.3. Reaction (3): channels of forming four-membered Siheterocyclic ring silylene (INT3) and

Its isomer (P3), H-transfer product (P3.1) and Me-transfer products (P3.2 and P3.3)

The geometrical parameters of the four-membered Si-heterocyclic ring silylene (INT3), transition states (TS3, TS3.1, TS3.2 and TS3.3) and products (P3, P3.1, P3.2 and P3.3) appearing in reaction (3) between Me₂Si=Si: and acetaldehyde are given in Fig. 4. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. According to Fig. 2, it can be seen that reaction (4) consists of five steps: the first step is that the two reactants (R1, R2) form a four-membered Si-heterocyclic ring silylene (INT3), which is a barrier-free exothermic reaction of 181.6 kJ/mol; the second step is that the INT3 isomerizes to a distorted four-membered ring product (P3) through the transition state (TS3) with energy barrier of 7.3 kJ/mol; the third step is that the four-membered Si-heterocyclic ring silvlene (INT3) undergoes C(3)—Si(2) hydrogen transfer via the transition state TS3.1 with energy barrier of 10.5 kJ/mol, resulting in the formation of product (P3.1); the fourth and fifth steps are

that the four-membered Si-heterocyclic ring silylene (INT3) undergoes Si-Si and C(3)-Si(2) methyl transfer via the transition states TS3.2 and TS3.3 with energy barriers of 53.1 and 67.2 kJ/mol, respectively, resulting in the formation of products (P3.2 and P3.3). The reaction of INT3 \rightarrow P3.2 is prohibited in thermodynamics because the energy of P3.2 is 16.2 kJ/mol higher than that of INT3. The reaction of $INT3 \rightarrow P3$ is the dominant reaction pathway the reaction (3) because the energy barrier of TS3 are 3.2 and 59.9 kJ/mol lower than TS3.1 and TS3.3. According to Figs. 1, 2 and 4 and statistical thermodynamics formula: $P_{\rm T}(i) = \frac{e^{-\Delta G_{\rm T}(i)/RT}}{\sum_i e^{-\Delta G_{\rm T}(i)/RT}}$ and $\Delta G_{\rm T}(i) = -RT \ln K_{\rm i}$, it can be seen that INT1 and INT3 are isomerized, $R1 + R2 \rightarrow INT1$ and $R1 + R2 \rightarrow INT3$ are two parallel reactions, the equilibrium distributions of INT1 and INT3 are $P_{T}(INT1) = K(INT1)/[K(INT1) + K(INT3)]$ $P_{\rm T}({\rm INT3}) = K({\rm INT3})/[K({\rm INT1}) + K({\rm INT3})] \approx 1.0,$ $\approx 0.0.$ respectively. So, INT3 is the main distribution.

3.4. Reaction (4): channel of forming a spiro-Si-heterocyclic ring compound (P4)

In reaction (4), the four-membered Si-heterocyclic ring silylene (INT3) further reacts with acetaldehyde (R2) to form a spiro-Si-heterocyclic ring compound (P4). The geometrical parameters

Reaction	Species	ZPE	B3LYP/6-31G*	
			$^{a}E_{\mathrm{T}}$	E _R
^b Reaction (1)	R1 + R2	0.13075	-812.43277	0.0
	INT1	0.13293	-812.45857	-67.7
	TS1(INT1-P1)	0.13241	-812.44924	-43.2
	P1	0.13523	-812.51677	-220.5
	TS1.1(P1–P1.1)	0.13250	-812.45919	-69.4
	P1.1	0.13454	-812.49563	-165.0
	TS1.2(P1-P1.2)	0.12997	-812.47335	-106.5
	P1.2	0.13079	-812.49747	-169.9
	TS1.3(P1-P1.3)	0.13039	-812.48195	-129.1
	P1.3	0.13177	-812.49462	-162.4
^c Reaction (2)	P1 + R2	0.19105	-966.29107	0.0
	INT2	0.19289	-966.30564	-38.3
	TS2(INT2-P2)	0.19252	-966.29518	-10.8
	P2	0.19510	-966.33974	-127.8
^b Reaction (3)	R1 + R2	0.13075	-812.43277	0.0
	INT3	0.13435	-812.50193	-181.6
	TS3(INT3-P3)	0.13424	-812.49915	-174.3
	P3	0.13488	-812.50386	-186.6
	TS3.1(INT3-P3.1)	0.12962	-812.49792	-171.1
	P3.1	0.13073	-812.51803	-223.9
	TS3.2(INT3-P3.2)	0.13421	-812.4817	-128.5
	P3.2	0.13453	-812.49577	-165.4
	TS3.3(INT3-P3.3)	0.13216	-812.47635	-114.4
	P3.3	0.13240	-812.51159	-206.9
^d Reaction (4)	INT3 + R2	0.19017	-966.27623	0.0
	INT4	0.19283	-966.30325	-70.9
	TS4(INT4-P4)	0.19236	-966.29024	-36.8
	P4	0.19459	-966.3375	-160.9

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 B3LYP/6-31G* method.

 $\begin{array}{l} {}^{a} \ \, E_{\rm T} \, = \, E({\rm Species}) \, + \, {\rm ZPE.} \\ {}^{b} \ \, E_{\rm R} \, = \, E_{\rm T} - E_{({\rm R}1 \, + \, {\rm R}2).} \\ {}^{c} \ \, E_{\rm R} \, = \, E_{\rm T} - E_{({\rm P}1 \, + \, {\rm R}2).} \\ {}^{d} \ \, E_{\rm R} \, = \, E_{\rm T} - E_{({\rm INT}3 \, + \, {\rm R}2).} \end{array}$



Figure 2 The potential energy profile of the cycloaddition reactions between Me₂Si=Si: and MeHC=O with B3LYP/6-31G^{*}.



Figure 3 Optimized B3LYP/6-31G^{*} geometrical parameters of INT2, TS2, P2 and the atomic numbering for cycloaddition reaction (2). Bond lengths and bond angles are in angstrom and degree, respectively.



Figure 4 Optimized B3LYP/6-31G^{*} geometrical parameters of INT3, TS3, P3, TS3.1, P3.1, TS3.2, P3.2, TS3.3, P3.3 and the atomic numbering for cycloaddition reaction (3). Bond lengths and bond angles are in angstrom and degree, respectively.



Figure 5 Optimized B3LYP/6-31G^{*} geometrical parameters of INT4, TS4, P4 and the atomic numbering for cycloaddition reaction (5). Bond lengths and bond angles are in angstrom and degree, respectively.

of intermediate (INT5), transition state (TS4) and product (P4) appearing in reaction (4) are given in Fig. 5. The energies are listed in Table 1, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. According to Fig. 2, it can be seen that the process of the reaction (4) is as follows: on the basis of INT3 formed in the reaction (3), the INT3 further reacts with acetaldehyde (R2) to form an intermediate (INT4), which is also a barrier-free exothermic reaction of 70.9 kJ/mol; and then the intermediate (INT4) isomerizes to a spiro-Si-heterocyclic ring compound (P4) via the transition state (TS4) with an energy barrier of 34.1 kJ/mol. Compared reaction (4) with reaction (3), it is realizing that the two reactions compete mutually due to scrambling for INT3 together. In reaction (3), the energy barrier of INT3 \rightarrow P3 is 7.3 kJ/mol. However, in reaction (4), $INT3 + R2 \rightarrow P4$ can directly reduce the system energy of 70.9 kJ/mol. Therefore, reaction (4) should be the dominant reaction channel.

3.5. Theoretical analysis and explanation of the dominant reaction channel

According to the above analysis, reaction (4) should be the dominant reaction channel of the cycloaddition reaction between singlet Me₂Si=Si: and acetaldehyde. Namely:

$$R1 + R2 \longrightarrow INT_3 \xrightarrow{+R2} INT_4 \xrightarrow{TS4} P4$$
 Reaction (5)

In the reaction, the frontier molecular orbitals of R2 and INT3 are shown in Fig. 6. According Fig. 6, the frontier molecular orbitals of R2 and INT3 can be expressed in schematic diagram 7. The mechanism of the reaction could be explained with the molecular orbital diagram (Fig. 7) and Figs. 1, 4 and 5. According to Figs. 1 and 4, as Me₂Si=Si: initially interacts with acetaldehyde, the [2 + 2] cycloaddition of the bonding π orbitals firstly results in a four-membered Si-heterocyclic ring silvlene (INT3). Because INT3 is an active intermediate, so INT3 may further react with acetaldehyde (R2) to form a spiro-Si-heterocyclic ring compound (P4). The mechanism of the reaction can be explained with Figs. 5 and 7, when the INT3 interacts with acetaldehyde (R2), the 3p unoccupied orbital of the Si(2) atom in INT3 will insert the π orbital of acetaldehyde from the oxygen side, then the shift of π -electrons to the p unoccupied orbital forms a $\pi \rightarrow p$ donor-acceptor bond, leading to the formation of intermediate (INT4). As the reaction goes on, the $\angle C(5)O(2)Si(2)(INT2: 136.9^{\circ}, TS4:$ 98.5°, P4: 70.6°) decreases gradually, and the C(5)-O(2) bond(INT4: 1.253 Å, TS4: 1.273 Å, P4: 1.487 Å) gradually elongate, Finally, the Si(2) atom in INT4 hybridizes to an sp³ hybrid orbital after the transition state TS4, forming the stabler spiro-Si-heterocyclic ring compound (P4).



Figure 6 The frontier molecular orbitals of R2 and INT3.



Figure 7 A schematic interaction diagram for the frontier orbitals of INT3 and MeHC=O(R2).

4. Conclusion

On the basis of the potential energy profile the cycloaddition reaction between singlet Me₂Si=Si: and acetaldehyde obtained with the B3LYP/6-31G^{*} method can be predicted. This reaction has one dominant channel. It consists of three steps: the first step is that the two reactants (R1, R2) form a four-membered Si-heterocyclic ring silylene (INT3), which is a barrier-free exothermic reaction of 181.6 kJ/mol; the second step is that INT3 further reacts with acetaldehyde (R2) to form an intermediate (INT4), which is also a barrier-free exothermic reaction of 70.9 kJ/mol; the third step is that intermediate (INT4) isomerizes to a spiro-Si-heterocyclic ring compound (P4) via a transition state (TS4) with an energy barrier of 34.1 kJ/mol.

The π orbital of X₂Si=Si: (X = H, Me, F, Cl, Br, Ph, Ar...) and the 3p unoccupied orbital of Si: in X₂Si=Si:

(X = H, Me, F, Cl, Br, Ph, Ar...) are the object in cycloaddition reaction of X₂Si=Si: (X = H, Me, F, Cl, Br, Ph, Ar...) and the asymmetric π -bonded compounds. The [2 + 2] cycloaddition reaction between the π orbital of X₂Si=Si

and the asymmetric π -bonded compounds. The [2 + 2] cycloaddition reaction between the π orbital of X₂Si=Si: (X = H, Me, F, Cl, Br, Ph, Ar...) and the bonding π orbital of the asymmetric π -bonded compounds leads to the formation of the four-membered Si-heterocyclic ring silylene. The 3p unoccupied orbital of Si: atom in the four-membered Si-heterocyclic ring silylene further reacts with the bonding π orbital of the asymmetric π -bonded compounds to form a spiro-Si-heterocyclic ring compound.

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