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THEORETICAL STUDIES OF CARBENES AND CARBENOIDS. 5. INTRAMOLECULAR REACTIONS OF CYCLOPROPYLCARBENE[1]

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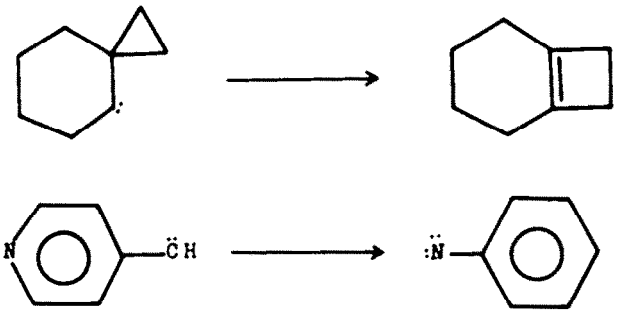
Abstract Intramolecular reactions of cyclopropylcarbene in singlet ground state have been studied using HF/3-21G gradient methods. Relative energies are estimated with 6-31G**. The "super-conjugation" between the cyclopropyl and the p AO at the carbene site stabilizes the carbene and retards its exo-endo isomerization with a barrier of 13.7 kcal/mol. The ring expansion occurs preferably from the exo conformation with a barrier of 12.9 kcal/mol. Two terminals disrotate in different rotation directions before and after the transition state. The ring expansion from the endo conformation is a more energetic pathway. The 1,2 H shift is not competitive to the ring expansion for its much higher barrier.

In carbene chemistry there are several well-known types of intramolecular reactions, such as ring openings[2], ring contractions[3], ring expansions[3], carbene-carbene rearrangements[4], and 1,2 hydrogen migrations, etc.[5-6]. The isomerization of cyclopropylcarbene 1 to cyclobutene 2 is typical of ring expansions of carbenes.

1a (exo conformation)
1b (endo conformation)

2

After discovering the reaction 1 to 2, there have been found a number of intramolecular reactions involving the ring expansion process of carbenes, for instances[7,8,5],



Now the ring expansion of carbenes has been utilized as a versatile route for general syntheses of cycloalkenes. The mechanistic and applicable studies of cyclopropylcarbenes have been the subject of several investigations[9]. The reaction is concerted at least for singlet carbenes. The ring expansions of substituted cyclopropylcarbenes are highly stereospecific. The reaction favors the migration of the less substituted and stronger carbon-carbon bond in the cyclopropane ring, which is explained with the steric interactions. The side reaction of cyclopropylcarbene to isolated ethylene and acetylene is more probable in gas phase than in solution. The dimerization of dicyclopropylcarbene strongly suggests that cyclopropyl substituents stabilize the carbene.

The only theoretical study of reaction 1 to 2 was performed with MINDO/3 method[10]. The calculation shows that the reaction of 1 to 2 is initiated by an electrophilic attack of the empty p AO at the carbene site on the most electron -rich carbon atom of the cyclopropane ring.

Since the reaction 1 to 2 has mostly been studied in experiments and no ab initio study reported, the ring expansion of cyclopropylcarbene is not well understood yet. The absence of the 1,2 hydrogen shift product remains to be a puzzle[9d]. Therefore the intramolecular reactions of the carbene require a thorough ab initio study with analytical gradient technique. The exo-endo isomerization, the ring expansion and the 1,2 hydrogen shift of the carbene in singlet ground state will be studied below. The fragmentation to ethylene and acetylene has been well understood[10] and will not be studied here.

Calculational Methods

The calculations are carried out using GAUSSIAN 80[11] system of programs. The MINDO/3 geometries[10] of 1a, 1b and the ring expansion transition states are taken as input parameters for optimizations. All related structures are fully optimized with analytical gradient techniques and 3-21G[12] basis set. The second order of derivative matrices of energy are calculated to characterize to structures. The larger basis set 6-31G**[13] is used to estimate the total and relative energies.

Results and Discussions

The equilibrium and transition structures are shown in Figure 1. The total and relative energies are listed in Table 1 and the net atomic charges in Table 2.

Carbene 1 The cyclopropylcarbene has two conformations, exo 1a and endo 1b, as shown in Figure 1. Both of the two conformations have C_s symmetry with a plane bisecting the cyclopropane ring and passing through the carbene center. The exo conformation is more stable than the endo one by 1.4 kcal/mol at 6-31G**. The most electron-rich carbon atom is that connecting to the carbene center (Table 2). The least negatively charged carbon atom is the carbene carbon. The group C_4H_6 has very little charge.

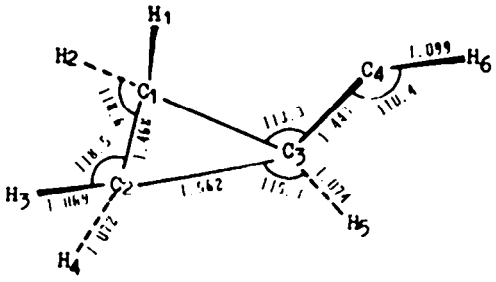
Carbene 1 in singlet ground state has a nonbonded σ orbital occupied by a pair of electrons at the carbene site. The p AO at the carbene site is the major component of the LUMO of 1. In the conventional concept the p AO is considered as an empty orbital. In fact, it is parallel to the cyclopropyl ring and the C_1-C_2 bond of the cyclopropyl, which results in the "super-conjugation" between the p AO and the cyclopropyl. The super-conjugation causes some charges transfered from cyclopropyl to this p AO, which is occupied by 0.15 electrons as shown by the Mulliken analyses at 3-21G. So the p AO is not a really empty orbital. The bond C_3-C_4 is 1.443Å in 1a and 1.445Å in 1b, being shorter than the single carbon-carbon bond and longer than the double carbon-carbon bond. The super

Table 1 Total energies (au) and relative energies(kcal/mol)

Structure	3-21G//3-21G		6-31G**//3-21G	
	Total	Relative	Total	Relative
1a	-153.93080	0	-154.81472	0
1b	-153.92791	1.8	-154.81245	1.4
2	-154.03072	-62.7	-154.90842	-58.8
3	-154.01872	-52.2	-154.89748	-51.9
4(1a→ 1b)	-153.90870	13.9	-154.79294	13.7
5a(1a→ 2)	-153.90889	13.7	-154.79423	12.9
5b(1b→ 2)	-153.87429	35.5	-154.76011	34.3
6a(1a→ 3)	-153.87450	35.3	-154.77312	26.1

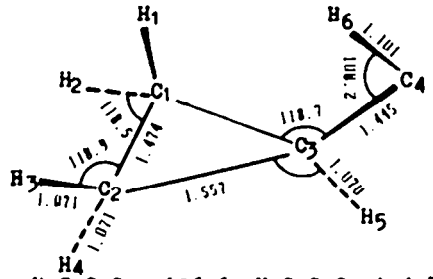
Table 2 Atomic charges calculated at the level of 6-31G**//3-21G

Atom	1a	1b	2	3	4	5a	5b	6a
C_1	-.221	-.239	-.243	-.288	-.275	-.309	-.344	-.299
C_2					-.250	-.217	-.244	-.277
C_3	-.309	-.297	-.134	.082	-.239	-.117	-.015	-.009
C_4	-.096	-.056		-.342	-.044	-.245	-.319	-.283
H_1	.161	.156	.122	.145	.133	.219	.177	.161
H_2	.149	.154			.137	.161	.170	.156
H_3					.142	.167	.158	.163
H_4					.138	.138	.137	.155
H_5	.134	.152	.132	.129	.169	.128	.148	.139
H_6	.079	.059			.090	.076	.132	.094



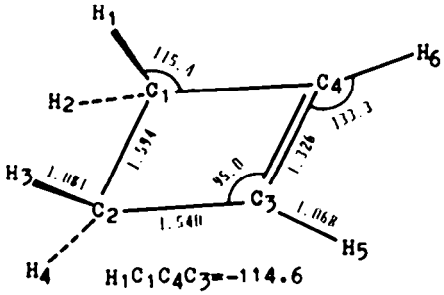
$H_1C_1C_2C_3$=-105.0, $H_2C_1C_2C_3$=104.0

1a (exo), C_s



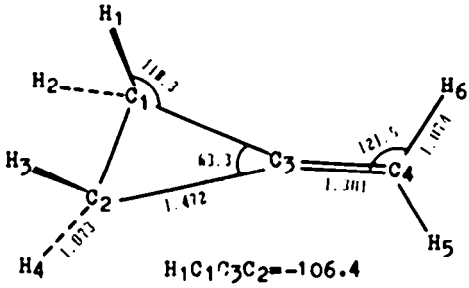
$H_1C_1C_2C_3$=-106.6, $H_2C_1C_2C_3$=104.3

1b (endo), C_s



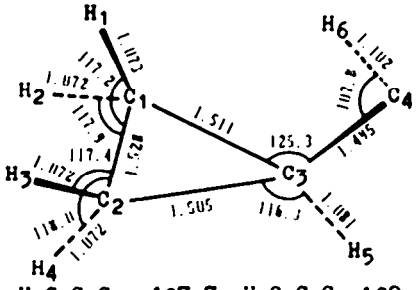
$H_1C_1C_4C_3$=-114.6

2, C_{2v}



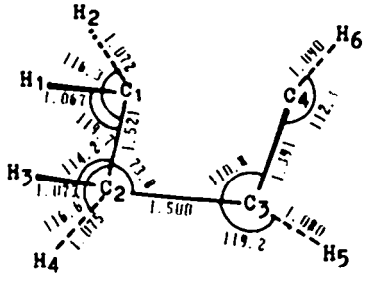
$H_1C_1C_3C_2$=-106.4

3, C_{2v}



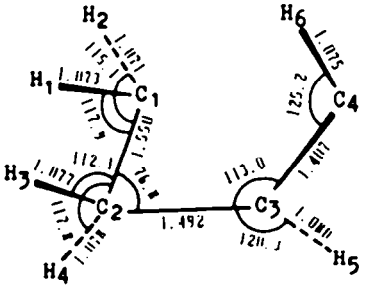
$H_1C_1C_2C_3$=-107.7, $H_2C_1C_2C_3$=108.6
$H_3C_2C_1C_3$=106.9, $H_4C_2C_1C_3$=-108.5
$H_5C_3C_1$=117.2, $C_4C_3C_2$=121.7
$H_6C_4C_3C_1$=-51.4

4 (1a → 1b)



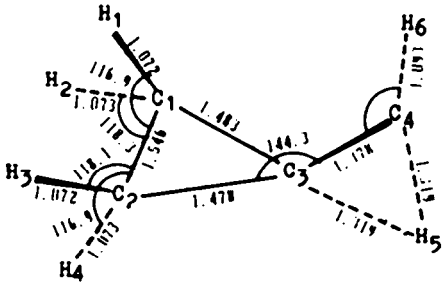
$H_1C_1C_2C_3$=-121.5, $H_2C_1C_2C_3$=104.3
$H_3C_2C_1C_3$=114.4, $H_4C_2C_1C_3$=-111.4
$H_5C_3C_2C_1$=-111.9, $C_4C_3C_2C_1$=51.2
$H_6C_4C_3C_2$=-153.9

5a (1a → 2)



$H_1C_1C_2C_3$=-127.5, $H_2C_1C_2C_3$=91.8
$H_3C_2C_1C_3$=112.1, $H_4C_2C_1C_3$=-114.4
$H_5C_3C_2C_1$=-121.4, $C_4C_3C_2C_1$=32.8
$H_6C_4C_3C_2$=53.6

5b (1b → 2)



$H_1C_1C_2C_3$=-106.5, $H_2C_1C_2C_3$=108.4
$H_3C_2C_1C_3$=105.8, $H_4C_2C_1C_3$=-109.5
$H_5C_3C_4C_1$=119.2, $C_4C_3C_2C_1$=-165.5
$H_6C_4C_3C_1$=-20.7

6a (1a → 3)

Figure 1 The 3-210 equilibrium and transition structures of cyclopropylcarbene and its isomerization species. Bond lenths are in Å and bond angles in degrees.

-conjugation also changes the chemical properties of the carbene. The occupation of the p AO enhances the LUMO, reduces the electrophility, and stabilizes the carbene. This analyses support the prediction from experiments[9c].

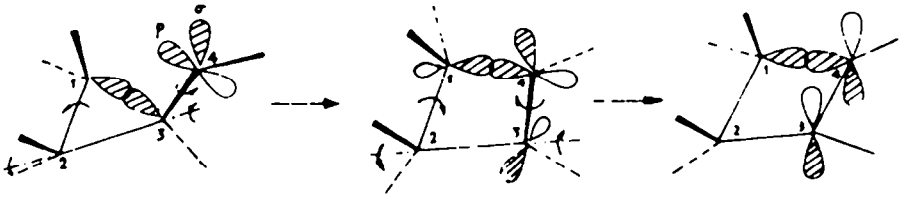
Exo-endo Isomerization The exo-endo isomerization occurs via the rotation of C_4-H_6 around the carbene bond C_3-C_4. The transition state is 4. The p AO at the carbene site in 4 is no longer parallel to C_1-C_2 bond and the carbon ring, and the super-conjugation between the p AO and the cyclopropyl disappears. The carbene bond C_3-C_4 in 4 is 1.495Å, being 0.05Å longer than that in 1. But the atomic charge on the carbene carbon in 4 is less than that in 1. Some charge has been transfered to the cyclopropyl from the group C_4H_6 in the process 1 to 4. The change of the atomic charge is consistent with the disappearance of the super-conjugation between the cyclopropyl and the p AO at the carbene site.

The rotation barrier is 13.7 kcal/mol at 6-31G**, which is larger than the rotation barrier of ethane[14] by about 10 kcal/mol at the same level mainly because of the super-conjugation in 1. So the rotation around the carbene bond in 1 is not as free as that around the single C-C bond in alkane.

Ring Expansion 1a→2 The ring expansion of cyclopropylcarbene to cyclobutene 2 may start from either exo conformation 1a or endo conformation 1b. Here we first discuss the former case. The process of 1a to 2 involves the rupture of C_1-C_3 (or C_2-C_3) bond in the ring and the formation of a new C_1-C_4 (or C_2-C_4) bond. The reaction barrier is 12.9 kcal/mol and the released energy is 58.8 kcal/mol at 6-31G**. The low barrier and the large released energy are in agreement with the easy isomerization in experiments[9].

The process of 1a to 2 (Scheme 1) is really a little complicated. As the carbene carbon C_4 moves to C_1, the bond C_1-C_3 is broken, two end C-C bonds disrotate inwards around the middle one so as to be co-planar, and the terminal methylene group and the carbene group disrotate to be "face to face". All these changes occur in concert. In transition state 5a, C_1-C_4 is 1.975Å, being 0.535Å shorter than that in 1a; C_1-C_3 is 1.813Å, being 0.251Å longer; the terminal methylene and the carbene groups have rotated nearly "face to face"; and the two end C-C bonds have rotated with 51.2 degrees away from being co-planar. After 5a, the two end C-C bonds continue to disrotate, but the carbene group and the terminal methylene group inverse their rotation directions, until the product 2 is formed. Both before and after the transition state, the two terminals disrotate but in different rotation directions. The methylene and the carbene groups have rotated for about 20 and 60 degrees, respectively, in this process.

Scheme 1



1a (exo) 5a (TS) 2

This reaction mechanism may be described with the interactions of frontier molecular orbitals (Scheme 1). The rupture of C-C bond leaves two singly occupied p AOs at C_1 and C_3. The disrotation of the two terminal groups favors the socalled LUMO-SOMO interaction between the p AOs at C_1 and C_4. So the p AO

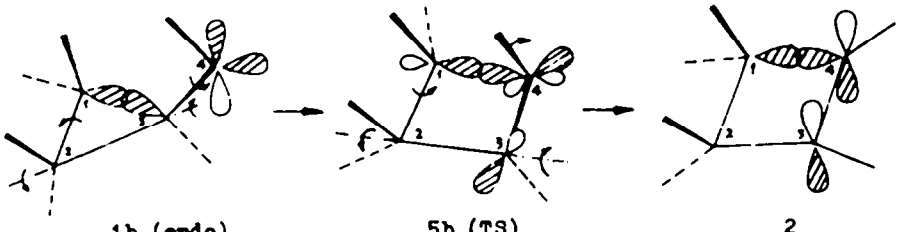
at the carbene site determines the way of the reaction before the transition state. The carbene angle $H_6C_4C_3$ in 5a is only 1.9 degrees larger than that in 1a, which indicates that the molecule still has some carbene character, the σ orbital at C_4 has not participated in the reaction yet. After 5a, the σ orbital takes part in the reaction, and the carbene group inverses its rotation direction to form a ground π orbital in 2. So this process is allowed by the orbital symmetry both before and after the transition state. The participation of the σ orbital at the carbene site results in changing the rotation direction of the carbene terminal.

The reaction of 1a to 2 involves two electrons from the fission of a C–C bond in the ring before the transition state, and four electrons thereafter including the σ electrons at the carbene site. Because the σ orbital at the carbene site has no relation to the formation of the π bond of 2, the reaction involves only two π electrons in the overall process. So the reaction may also be described with Hückel 4n+2 rule. The difference is that the rotation directions of the two terminals change after the transition state.

In 5a the Mulliken population between C_1 and C_3 is −0.03, and that between C_1 and C_4 is 0.10 at 3-21G. So C_1 is not bonded to C_3 but bonded to C_4 up to the transition state. The carbene carbon and the group C_4H_6 are both negatively charged to a considerable extent. They gain electrons mainly by the interaction between the p AOs at the carbene site and at C_1. The p AO at the carbene site is largely occupied in the transition state.

Ring Expansion 1b→2 The ring expansion starting from the endo conformation 1b occurs via transition 5b. The reaction barrier is 32.9 kcal/mol and the released energy is 60.2 kcal/mol at the 6-31G** level. The reaction mechanism in the early stage is similar to that of 1a to 2. As bond C_1–C_3 is broken, two end C–C bonds disrotate around the middle one in order to be co-planar, and the two terminals disrotate in favor of the attack of the p AO at the carbene site on C_1. In transition state 5b, the angle $H_6C_4C_3$ has been expanded to 125.2 degrees from 108.2 degrees, being only smaller than that in 2 by 8.1 degrees. The new bond C_1–C_4 is 1.874Å, being 0.334Å larger than that in 2. The new 4-membered ring is from being co-planar by 32.8 degrees. The strangely large angle $H_6C_4C_3$ in 5b is in concordance with the high reaction barrier.

Scheme 2



1b (endo) 5b (TS) 2

The reaction mechanism after the transition state is entirely different from that starting from the exo conformation. Because the angle $H_6C_4C_3$ in 5b is very large, and the C_1–C_4 bond and the new 4-membered carbon ring are nearly formed, the carbene terminal C_4H_6 is highly strained from rotation. So the reaction after 5b is unable to proceed via the rotation of C_4–H_6 around bond C_3–C_4. It is more likely, then, to proceed via bending bond C_4–H_6 toward being

coplanar with the carbon skeleton. The reason is clear. If the reaction after 5b proceeds via rotating C_4-H_6 around C_3-C_4 in the previous direction, the responded π MO formed between C_3 and C_4 in 2 must be an excited MO. So the continuous rotation of C_4-H_6 around C_3-C_4 is not orbital symmetry allowed.

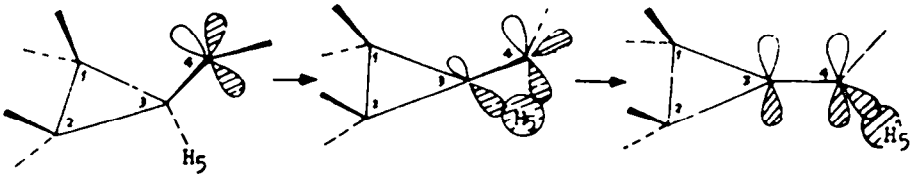
After the early stage before 5b in Scheme 2, the reaction is already a bit different from that of 1a to 5a. Although the initial LUMO-SOMO interaction between C_1 and C_4 favors the reaction, the continuous rotations of terminals are retarded by the different phase interaction between the p AOs at C_3 and C_4. The reaction then is led to a pathway different from that of 1a to 2 so as to avoid an excited π MO formed. Transition state 5b is much later than that of 1a to 2 as shown by the larger angle $H_6C_4C_3$, the smaller dihedral angle $H_6C_4C_3C_2$, and the shorter bond C_3-C_4.

The ring expansion directly from 1b is unlikely to occur in experiment. If the carbene is yielded in the endo conformation initially, it is more likely to rearrange to the exo conformation first, and then isomerize to cyclobutene via a ring expansion process shown in Scheme 1.

1,2 Hydrogen Shift 1→3 The 1,2 hydrogen migration also may start from either the exo conformation or the endo conformation. The reaction mechanisms from the two conformation may be similar because of the same orbital symmetries. Here only the hydrogen shift from the ground conformation 1a is discussed.

The 1,2 hydrogen migration from 1a occurs via transition state 6a. The reaction barrier is 26.1 kcal/mol and the released energy is 53.3 kcal/mol at 6-31G**. From 1a to 6a, the hydrogen H_5 moves to the p AO at the carbene site, as shown in Scheme 3. C_4-H_6 rotates around C_3-C_4 simultaneously in favor of the largest interaction between H_5 and the p AO. Up to 6a, the new C-H bond has been partly formed, the old C-H bond partly broken, and C_4-H_6 has rotated with 20.7 degrees away from being co-planar with the cyclopropane ring. After 6a, the migrated hydrogen moves into the σ orbital at the carbene site to form 3.

Scheme 3



The rearrangement of 1 to 3 is not a competitive reaction to the ring expansion. Firstly the fission of the C-H bond is more difficult than that of a C-C bond in such a strained ring. Secondly the rotation of C_3-H_5 is strained by the steric interactions in molecule, and the rotation of C_4-H_6 is retarded by the super-conjugation between the cyclopropyl and the p AO at the carbene site.

Summary

(1) The super-conjugation between the cyclopropyl and the p AO at the carbene site stablizes the carbene and retards itsexo-endo isomerization.

(2) The ring expansion is more likely to occur starting from the exo conformation. Two terminals disrotate with their rotation directions changed after the transition state. The reaction is electrophilic and stereospecific.

(3) The ring expansion from the endo conformation is hindered by the orbital symmetry.

(4) The 1,2 hydrogen migration is not competitive to the ring expansion from the exo conformation for its much higher energy barrier.

The above conclusions are generally valid even if electron correlation is taken into account. The correlated calculations may result in larger bond lengths and lower energy barriers[15-17], but the reaction mechanisms and the order of barriers of different routes are rarely changed for intramolecular reactions on the singlet ground energy surface. Of course, further studies including electron correlation are expected to appear.

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