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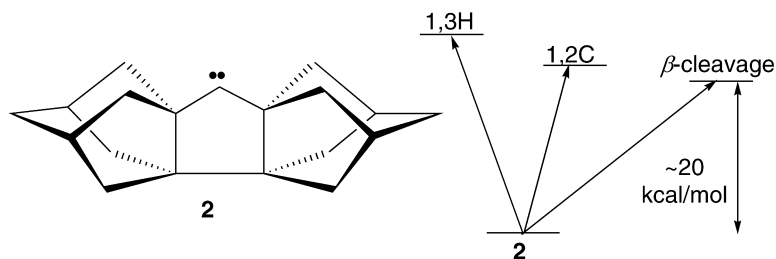
Singlet Hydrocarbon Carbenes with High Barriers Toward Isomerization: A Computational Investigation

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Singlet Hydrocarbon Carbenes with High Barriers Toward Isomerization: A Computational Investigation

Athanassios Nicolaides*

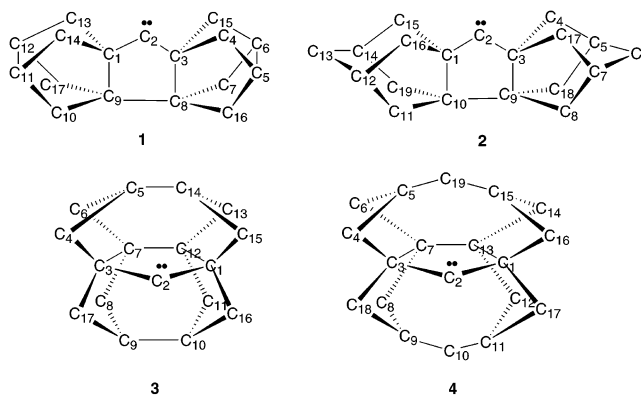*Contribution from the Department of Chemistry, University of Cyprus, Nicosia 1678, Cyprus*

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Abstract: A prerequisite for a stable singlet hydrocarbon carbene is the existence of high barriers toward isomerization. Four derivatives of cyclopentylidene (**1**−**4**) with rigid and varying carbon cages are examined computationally at the B3LYP/6-311+G(d,p) level of theory. Singlet ground states are predicted for carbenes **1**−**4**, with ΔE_{ST}'s = 7−22 kcal/mol. The rearrangement paths considered are 1,3-hydrogen shift, 1,2-carbon shift and β-CC bond-cleavage. Carbenes **3** and **4** lie in relatively shallow potential-energy wells (around 4 and 6 kcal/mol, respectively) and are expected to rearrange via 1,3-hydrogen shifts to cyclopropane derivatives. For **1** and **2**, the lowest energy rearrangement path is β-CC bond-cleavage requiring about 12 and 20 kcal/mol, respectively, placing **2** in the deepest potential-energy well among the four carbenes.

Usually, carbenes are thought of as reactive intermediates with short lifetimes.[1] However, recent efforts have transformed some of them to relatively stable, even isolable, species. Long-lived triplet carbenes have been generated with the help of bulky substituents that confer kinetic stabilization.[2] Stable singlet carbenes have been obtained by thermodynamically stabilizing the carbene center with heteroatoms.[3−5] However, to what extent these species can be considered as "pure" carbenes has been a matter of debate, because the ylidic character, as a result of the heteroatom, should not be neglected.[6] A stable singlet carbene without heteroatom stabilization is not yet known and the pursuit of such a species has been described as "an exciting and realistic goal".[3b]

One prerequisite for a stable singlet hydrocarbon carbene is the existence of high barriers toward internal rearrangements. To gain insight into possible structural requirements for such species heptacyclo[9.2.1.1³,⁶.1⁵,⁸.1⁹,¹².0¹,⁹.0³,⁸]-heptadec-2-ylidene (**1**), heptacyclo[10.3.1.1³,⁷.1⁵,⁹.1¹⁰,¹⁴.0¹,¹⁰.0³,⁹]-nonadec-2-ylidene (**2**), heptacyclo[8.4.1.1⁵,¹³.1⁶,¹².0¹,⁵.0³,⁸.0⁶,⁷]-heptadec-2-ylidene (**3**) and heptacyclo[9.5.1.1³,⁹.1⁵,¹⁵.0¹,¹³.0³,⁷.0⁷,¹³]-nonadec-2-ylidene (**4**) were explored computationally.

Computational Methods. All computations were performed with Gaussian98.[7] Geometries were optimized and the stationary points were characterized by vibrational analysis at the B3LYP/6-31G(d) level of theory.[8] Single-point B3LYP/6-311+G(d,p) energies at the optimized geometries were also obtained. Zero-point vibrational energies (ZPE) were scaled by 0.981.[9] Thus,

(1) See, for example: (a) Kirmse, W. In *Carbene Chemistry*; Academic Press Inc.: New York, 1964. (b) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols I and II. (c) Wentrup, C. In *Reactive Molecules*; Wiley-Interscience: New York, 1984. (d) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990. (e) Jones, Jr. M. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, pp 77−96. (f) Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, pp 132−174. (g) Bertrand, G., Ed.; *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*; Marcel Dekker: Netherlands, 2002.
(2) (a) Tomioka, H. *Acc. Chem. Re*s. **1997**, *30*, 1315. (b) Tomioka, H. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol 2, pp 175−214. (c) Tomioka, H.; Watanabe, T.; Hattori, M.; Nomura, N.; Hirai, K. *J. Am. Chem. Soc.* **2002**, *124*, 474.
(3) (a) Arduengo A. J. *Acc. Chem. Res.* **1999**, *32*, 913. (b) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
(4) (a) Despagnet, E.; Gornitzka, H.; Rozhenko, A. B.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 2835. (b) Sole, S.; Gornitzka, H.; Schoeller, W. W.; Bourissou D.; Bertrand G. *Science* **2001**, *292*, 5523.
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(6) (a) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674. (b) Heinemann, C.; Müller, T. Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (c) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039.
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(9) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16 502.

Table 1. Singlet (SE(S)) and Triplet (SE(T)) Stabilization Energies and Singlet−Triplet Splittings (ΔE_{S-T}) for Carbenes **1**−**5**[a,b]

	c	SE(S)	SE(T)	ΔE_{S-T}[d]
(1)	**1**(S/T) + CH_4 → **1**−H_2 + CH_2 (S/T)	33.6	16.3	6.8
(2)	**2**(S/T) + CH_4 → **2**−H_2 + CH_2 (S/T)	32.2	15.3	6.5
(3)	**3**(S/T) + CH_4 → **3**−H_2 + CH_2 (S/T)	55.3	23.2	21.7
(4)	**4**(S/T) + CH_4 → **4**−H_2 + CH_2 (S/T)	40.6	19.8	10.3
(5)	**5**(S/T) + CH_4 → **5**−H_2 + CH_2 (S/T)	32.7	12.0	10.2

[a] B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) +ZPE, unless otherwise noted.[4,15] [b] Units in kcal/mol. [c] **5**−H_2 symbolizes cyclopentane, and similarly for **1**−**4**, the extension "H_2" signifies the corresponding alkane. [d] A correction of 1.2 kcal/mol has been applied, so that ΔE_{S-T}(**5**) at this level of theory becomes 10.2 kcal/mol. (See "Computational Methods" section).

Table 2. Selected Geometrical Characteristics (R in Å and θ in deg) of Carbenes **1**−**5**[a,b]

	R_α	R_β	R_γ	θ_1	θ_2
1	1.469 (1.464)	1.664	2.911	105.0 (118.5)	119.5
2	1.479 (1.473)	1.622	2.708	105.6 (118.9)	114.0
3	1.466 (1.444)	1.599	2.315	105.8 (118.6)	97.7
4	1.477 (1.462)	1.598	2.476	106.6 (120.3)	105.9
5	1.492 (1.491)	1.550	3.006	102.9 (115.9)	97.3

[a] B3LYP/6-31G(d). Values in parentheses are for triplet states the others for the singlets. [b] R_α, R_β: α-CC and in-plane β-CC bond lengths. R_γ: distance between divalent C and nearest β-hydrogen. θ_1: bond-angle of divalent C. θ_2: angle formed by α-CC and out-of-plane β-CC bonds.
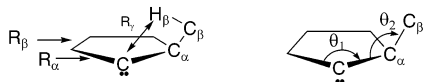
unless otherwise specified, relative energies used in the text are derived from B3LYP/6-311+G(d,p) energies and include scaled ZPE corrections.

For singlet−triplet (S−T) splittings, the convention E(T)−E(S) is used, i.e., positive splittings denote singlet ground-states. The S−T splitting of cyclopentylidene (**5**) was computed at the G3(B3LYP)[10] level of theory (9.7 kcal/mol, Table S2 of Supporting Information). However, at this level of theory the S−T splitting of methylene, which is known accurately from experiment,[11] is underestimated by 0.5 kcal/mol. It has been assumed that the same is true for **5**, so that a better estimate for ΔE_{ST}(**5**) is 10.2 kcal/mol. This value has been used to calibrate the S−T splittings of carbenes **1**−**4**, because for these carbenes G3(B3LYP) would be computationally too expensive. ΔE_{ST}(**5**) was computed 9.0 kcal/mol at the standard level of theory of this work (B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) + ZPE). Accordingly, the computed S−T splittings of **1**−**4** were increased by 1.2 kcal/mol, and these "corrected" values are reported in Table 1.

Results and Discussion

Carbenes **1**−**4** are derived formally from cyclopentylidene (**5**)[12] by substituting all eight hydrogens with hydrocarbon bridges. For each carbene, a "central" five-membered ring can be defined[13] with a plane of symmetry containing it. Fused to the central ring are four five-membered rings, each one sharing

an edge with it. These rings are linked pairwise either directly (**1** and **3**) or via one-methylene bridges (**2** and **4**). The linked rings lie on opposite sides of the symmetry plane (**1** and **2**) or on the same side (**3** and **4**). In the former case, the linking bridge is referred to as "perpendicular" and in the latter as "parallel".

Carbenes **1**−**5** are predicted to have singlet ground-states (Table 1).[14] The S−T splittings of carbenes **1**, **2**, and **4** are roughly the same as that of **5**, but ΔE_{ST}(**3**) is more than twice as large. Interestingly, the local geometry of the divalent carbon of **3** (as judged by R_a and θ_1, Table 2) is essentially the same as that of **1**, **2**, and **4**, which in turn is not that different from the parent **5**.
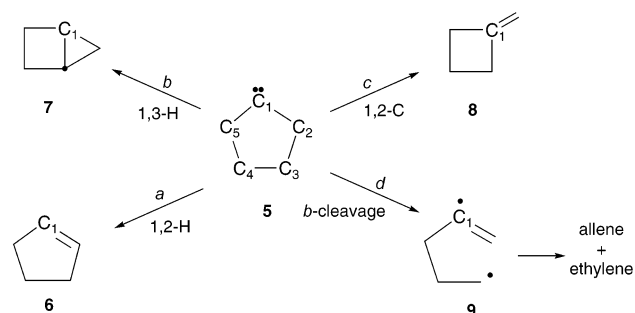
To gain insight into this difference, the isodesmic reactions shown in Table 1 were considered. The energies of these reactions assess the relative stabilization conferred by the alkyl substituents on carbenes **1**−**5**, with respect to the unsubstituted parent methylene.[15] For carbene **5**, the stabilization energy of its singlet state is more than twice as large as that of its triplet. This can be attributed to hyperconjugation, because this effect stabilizes more the singlet state (which is isoelectronic to a carbocation) than the triplet (which is more like a radical).[15,16a] Preferential stabilization of the singlet state with respect to the triplet, is also computed for carbenes **1**−**4**. The data of Table 1 show that the high value of ΔE_{ST}(**3**) is mainly due to the much higher stabilization of singlet **3** as compared to the singlets of the other carbenes. This is compatible with the hyperconjugation argument, since among **1**−**4**, θ_2 of carbene **3** is closest to 90°. This implies that the overlap between the formally vacant p orbital of the carbene and the orbital of β-CC bond is maximal for **3** and, therefore, hyperconjugation is most efficient in this case.[17]

Dialkyl carbenes usually have short lifetimes in part due to very fast internal rearrangements. Generally, three paths are available: (a) 1,2 hydrogen-, (b) 1,3 hydrogen-, and (c) 1,2 carbon shift. For acyclic carbenes the most favored path is *a*, unless they lack α-hydrogens. Cyclic carbenes are more complex, because a rigid carbon framework may favor other paths.[16a] 2-Norbornylidene[16a,b] prefers the 1,3 hydrogen shift to form nortricyclane, and cyclobutylidene[16c,d] isomerizes via paths *a* and *c*. In rare cases, a fragmentation path may also become dominant. For example, cyclobutenylidene[16e,f] ring-opens to vinylacetylene, presumably via a butadienylidene intermediate. The computed barriers for the four paths (*a*−*d*) for **5** (Scheme 1) are 5.7, 27.5, 51.1, and 36.0 kcal/mol, respectively.[18]

Path *b* for carbenes **1**−**4** gives substituted cyclopropanes **10**−**13**, respectively. In each case there are two classes of β-hy-

(10) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.

(11) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Phys. Chem.* **1983**, *79*, 5251.

(12) Xu, G.; Chang, T.-M.; Zhou, J.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1999**, *121*, 7150.

(13) These are C_1−C_2−C_3−C_8−C_9 in **1**, C_1−C_2−C_3−C_9−C_{10} in **2**, C_1−C_2−C_3−C_7−C_{12} in **3** and C_1−C_2−C_3−C_7−C_{13} in **4**.

(14) Dialkylcarbenes usually have singlet ground-states. For notable exceptions, see: (a) Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. *J. Am. Chem. Soc.* **1982**, *104*, 2326. (b) Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232. (c) Iiba, E.; Hirai, K.; Tomioka, H.; Yoshioka, Y. *J. Am. Chem. Soc.* **2002**, *124*, 14 308.

(15) Hehre, W. J.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(16) (a) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F.; Hadad, M. *J. Am. Chem. Soc.* **1997**, *119*, 5682. (b) Kirmse, W.; Meinert, T.; Modarelli, D. A.; Platz, M. S.; *J. Am. Chem. Soc.* **1993**, *115*, 8918. (c) Pezacki, J. P.; Pole, D. L.; Warkentin, J. Chen, T.; Ford, F.; Toscano, J.; Fell, J.; Platz, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 3191. (d) Stracener, L. L.; Halter, R. J.; McMahon, R. J.; Castro, C.; Karney, W. L. *J. Org. Chem.* **2000**, *65*, 199. (e) Dyer, S. F.; Kammula, S.; Shevlin, P. B. *J. Am. Chem. Soc.* **1977**, *99*, 8104. (f) Nicolaides, A.; Matsushita, T.; Tomioka, H. *J. Org. Chem.* **1999**, *64*, 3299.

(17) The singlet states of carbenes **3** and **5** are not expected to have the same stabilization energy, because hyperconjugation in the former case involves C−C bonds, and in the latter C−H bonds.

(18) At the B3LYP/6-311+G(d) level of theory, from ref 12.

Scheme 1. Isomerization Paths of **5**

Table 3. Barriers and Heats of Reactions for Isomerizations of Carbenes **1**−**5**[a−c]

	1,3H	1,2C[d]	β-CC cleavage
1	43.5 [−2.9]	25.2 [12.3]	12.1 [−6.8]
2	26.8 [−24.6]	24.1 [11.3]	19.9 [13.2]
3	4.3 [−64.9]	8.3 [−32.5]	36.2 [35.5]
4	6.3 [−57.5]	15.9 [−7.0]	31.1 [28.3]
5[e]	27.5 [−32.1]	51.0 [−44.0]	36.0 [18.9]

[a] B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) +ZPE, unless otherwise noted.[4,15] [b] Units in kcal/mol. [c] Heats of reactions in square brackets. [d] Out-of-plane β-CC migration for **1**−**4**, but in-plane β-CC for **5**. [e] From ref 12 (B3LYP/6-311+G(d) + ZPE).

drogens, but the proximal one is predicted to migrate preferentially. For example, in [1]**1** the distances of the β-hydrogens from the carbene center are 2.911 ($R_γ$ in Table 2) and 3.048 Å and the corresponding transition states (**TS(1−10)** and **TS2-(1−10)**) lie 43.5 and 65.9 kcal/mol, respectively, higher in energy (Table S1). The barriers for these H-migrations decrease as the reactions become more exothermic and as the distance ($R_γ$) of the migrating hydrogen from the divalent center decreases (Table 3). For [1]**3** and [1]**4** this is the lowest energy isomerization path, suggesting that attempts to prepare carbenes **3** and **4** may give instead cyclopropane derivatives **12** and **13**, respectively.

10, n=0
11, n=1

12, n=0
13, n=1
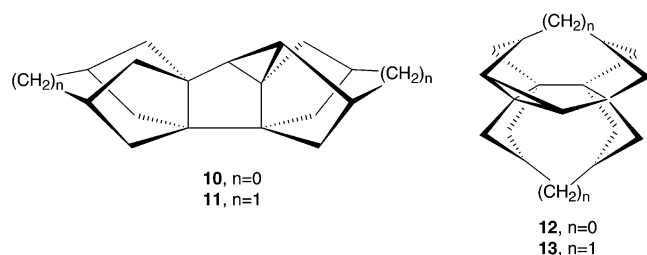
By symmetry two possible 1,2 carbon-shifts for carbenes **1**−**4** exist. Thus, (in-plane) migration of either β-carbon of the central ring is expected to give methylenecyclobutanes **14**−**17**, respectively. This path is analogous to *c* for **5**. According to the computed optimized geometries of **14**−**17**, these are strained bridgehead olefins (anti-Bredt olefins).[19] In this respect, structures **14**−**17** are somewhat misleading, because the depicted π bond is highly twisted and the molecules exhibit strong diradical character. This is reflected into the rather long bond between the olefinic carbons, which in the case of **14** is 1.45 Å.[20] To locate the transition state structures for the in-plane β-carbon migration, a series of partial optimizations, while varying systematically $R_β$ (as defined in Table 2), were carried out. The points of maximum energy along these paths were located and characterized as first-order saddle-points by frequency calculations. However, inspection of the eigenvectors of the imaginary frequencies, suggests that these points correspond to transition states connecting methylenecyclobutanes **14**−**17** with the corresponding diradicals **22**−**25**, rather than with carbenes **1**−**4**. It seems, then, that direct isomerization of carbenes **1**−**4** to the corresponding methylenecyclobutanes requires more energy than their stepwise isomerization via diradicals **22**−**25**. This finding is compatible with the high barrier (>50 kcal/mol) computed for the 1,2-C migration of the parent **5**.[12]

(19) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067.
(20) By comparison the length of the CC double bond of the isomeric diradical **22** is 1.32 Å.

The lack of "direct" transition states between carbenes **1**−**4** and the corresponding methylenecyclobutanes (**14**−**17**) may be understood qualitatively, if the reverse reaction (ring-opening of the methylenecyclobutanes), is considered. Isomerization of **14** to **1**, implies that during the C_2−C_3 bond-cleavage (of **14**), carbon C_1 will be moving "inwards" to form the new σ bond (between C_1 and C_3), introducing, thus, more strain into the corresponding transition state. In contrast, isomerization of **14** to diradical **22** requires simple cleavage of the C_2−C_3 bond, while the "exo" orientation of the C_1−C_3 bond is more or less retained during the transformation. The cleavage of the C_2−C_3 bond (in **14**) is not as difficult as it may appear at first sight, because the twisted geometry of the olefin allows for significant overlap between the p orbital of C_1 and the σ orbital of the C_2−C_3 bond and it is conceivable that as C_2−C_3 breaks, the π bond of the corresponding diradical (**22**) is formed in a smooth fashion.

14, n=0
15, n=1

16, n=0
17, n=1

18, n=0
19, n=1

20, n=0
21, n=1

22, n=0
23, n=1

24, n=0
25, n=1
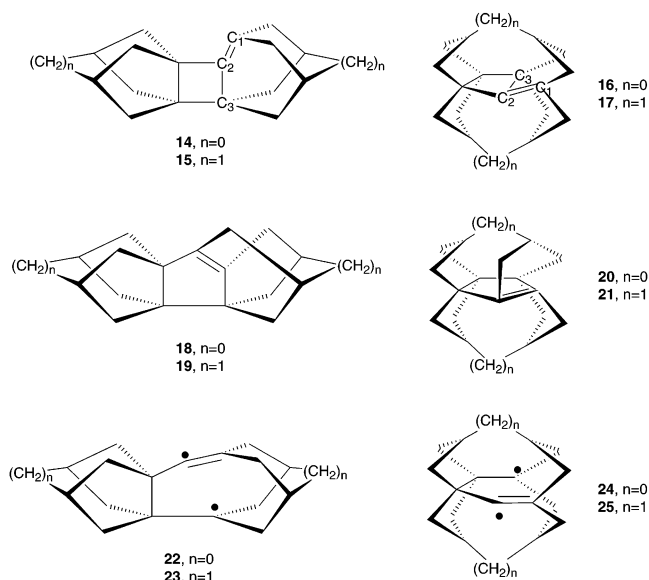
Out-of-plane β-carbon migration in carbenes **1**−**4** (path 1,2-C in Table 1), forms the bridgehead olefins **18**−**21**, respectively. In some respects this is similar to path *a* for **5**. Because this isomerization path involves the transfer of an exocyclic $C_αC_β$ bond to the carbene center, it is expected that the better the overlap between the orbital of the migrating bond and the formally vacant p orbital at the carbene center, the lower the barrier of the transformation. As mentioned above, a decrease in the bond-angle $θ_2$ corresponds to an increase in the orbital overlap, and indeed the barrier is computed to decrease as $θ_2$ decreases. Thus, in **1**−**4** the relative barriers of this isomerization follow the relative stabilization of the singlet state of the carbene.

Opening of the central ring of **1**−**4** by in-plane β-CC cleavage leads to the formation of diradicals **22**−**25**, respectively.[21] The barriers are significant for **3** and **4**, possibly because the parallel bridges tend to keep the central ring together. In contrast, the barrier for **1** is about one-third these values, presumably because of the small perpendicular bridge that strains the (in-plane) β-CC bond.[22] As mentioned above diradical **22** can conceivably isomerize to methylenecyclobutane **14**, but this requires a significant barrier (23.8 kcal/mol). On the contrary, **22** is expected to give triene **26** essentially without a barrier.[23] Triene **26** lies 42.9 kcal/mol lower in energy than diradical **22** and contains an allenic moiety, which is bent (by 160° and 147° in its singlet and triplet states, respectively). It has a singlet ground-state and an S−T gap of 6.2 kcal/mol, in agreement with other calculations for planar allene.[24] On the triplet surface, the transition state for the isomerization of ^{3}**1** to ^{3}**22** is 5.5 kcal/mol higher in energy than carbene ^{3}**1**. When the S−T gap of **1** (6.8 kcal/mol) is taken into account this transition state has almost the same energy (with respect to ^{1}**1**) as the corresponding one on the singlet surface.

26, n=0
27, n=1
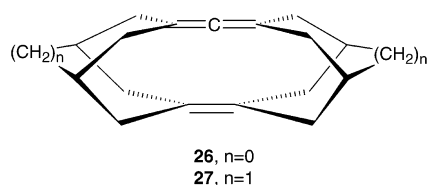
This isomerization places **1** in a relatively shallow potential-energy well of about 12 kcal/mol, and its isolation even at low temperature would be a challenging task. Furthermore, attempts to prepare **1** are likely to give triene **26** or products derived from it. Due to the modest ΔE_{S-T}(**1**) it is possible that products from its triplet state are formed also. In either case significant deviation from the usual chemistry of dialkylcarbenes is likely to be observed.

The profile of the in-plane β-CC cleavage for **2** is similar to that for **1**, in the sense that the barrier required for the formation of the diradical **23**, is higher than the barrier between **23** and triene **27**. However, in this case diradical **23** is higher in energy than carbene **2** (by 13.2 and 8.2 kcal/mol on the singlet and triplet surface, respectively) increasing the barrier for its formation to 19.9 kcal/mol on the singlet surface. On the triplet surface this barrier is 12.5 kcal/mol with respect to ^{3}**2** or 19.0 kcal/mol with respect to ^{1}**2**. Diradical **23** is predicted to give

Scheme 2. Isomerization Paths of Singlet **2**
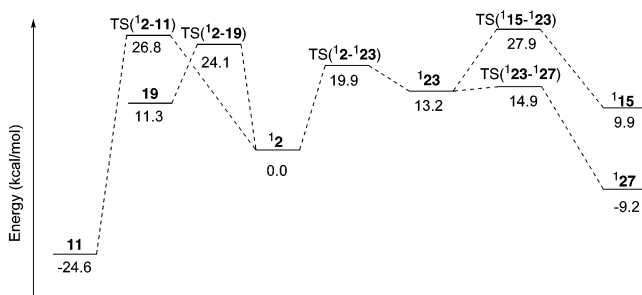
easily triene **27**, requiring 1.7 and 3.9 kcal/mol on the singlet and triplet surface, respectively. Allene **27** is bent by 165° and 153° in its singlet and triplet states, respectively and has a singlet ground-state with an S−T gap of 7.1 kcal/mol.

The isomerization of **2** to biradical **23** and subsequently to allene **27** is the lowest-energy rearrangement path of **2**, placing it in a potential-energy well which is the deepest among the four carbenes. In addition, this well is deep enough, that, in principle carbene **2** should be observable, at least at low temperature. Carbene **2** is an attractive synthetic target for a pure hydrocarbon carbene with a reasonably long lifetime. The barriers of the isomerization paths considered for **1**−**4**, follow closely the exothermicities of the corresponding reactions. This can be attributed to the rigid cyclopentane subunits and the variation in the lengths of the (perpendicular or parallel) bridges. These factors allow for geometrically well-defined and systematically varied carbon cages, an approach that has been applied also in the study of pyramidalized alkenes.[25]

Conclusion

Among the four carbenes, **2** is the most robust with respect to rearrangement. It is expected to be isolable at low-temperature in an inert matrix, and perhaps observable under ambient conditions. In the latter case, products derived from the β-CC cleavage of **2** may compete with those from its intermolecular chemistry. Due to the small S−T splitting of **2**, its triplet state should be thermally accessible under various experimental conditions. Thus, **2** constitutes an interesting synthetic target for exploring physical organic concepts of dialkyl carbenes. Finally, modifications of **2** that will increase the depth of its potential-energy well and improve its inherent stability are currently being sought.

(21) Out-of-plane β-CC cleavage requires more energy than the in-plane cleavage by 11.6 and 13.6 kcal/mol for **1** and **2**, respectively.
(22) R_β is 0.06 Å longer in **1** than in **3** and **4**
(23) The barrier is less than 0.01 kcal/mol before ZPE correction at the B3LYP/6-31G(d) level of theory.
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