

# Hydrogen Migration vs Carbon Migration in Dialkylcarbenes. A Study of the Preferred Product in the Carbene Rearrangements of Ethylmethylcarbene, Cyclobutylidene, 2-Norbornylidene, and 2-Bicyclo[2.1.1]hexylidene

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**Abstract:** Ethylmethylcarbene (**1**), cyclobutylidene (**2**), 2-norbornylidene (**3**), and 2-bicyclo[2.1.1]-hexylidene (**4**) and the transition states that correspond to 1,2-H-migration, 1,3-H-migration, and 1,2-C-migration were optimized at BHandHLYP/DZP, MP2/DZP, and CCSD(T)/DZP levels of theory. The 1,2-H-migration of **1** to 2-butene has a theoretically derived barrier of 5.2 kcal/mol at CCSD(T)/DZP. The 1,2-H-shift that leads to 1-butene has a  $\Delta G^\ddagger$  of 8.5 kcal/mol, 1,3-H-migration of 8.3 kcal/mol and 1,2-C-migration of 18.1 kcal/mol. For **2**  $\Delta G^\ddagger$  for 1,2-C-migration is only 10.5 kcal/mol, which is 7.6 kcal/mol less than for **1**. This lowering of the barrier for rearrangement of cyclobutylidene is attributed to the similarity between the TS and singlet **2** which prefers a nonclassical structure. The barrier for 1,2-H-migration for **2** is 9.7 kcal/mol due to H repulsion in the TS. For **3** the process with the lowest barrier (5.2 kcal/mol, BHandHLYP/DZP) is a 1,3-H-shift that leads to nortricyclene. The preference for this rearrangement can again be explained by the similarity between the carbene geometry and that of the corresponding TS that leads to the nortricyclene. For the rearrangement of **4**, which also resembles the TS for 1,3-H-migration, the corresponding TS has a  $\Delta G^\ddagger$  of 22.6 kcal/mol (BHandHLYP/DZP). The reason for this diverging behavior is the large amount of ring strain present in the TS for 1,3-H-migration of **4**. As a consequence, **4** is a long-lived, trappable carbene that rearranges slowly to form bicyclo[2.1.1]hex-2-ene ( $\Delta G^\ddagger = 16.2$  kcal/mol), while **3** can not be trapped with pyridine.

## Introduction

Today, our knowledge of reactive intermediates allows us to predict the course of many organic reactions. One of the most intriguing of these intermediates are carbenes. Discovered over 100 years ago<sup>2,3</sup> and systematically studied since about 1950,<sup>4–16</sup> their investigation is still a field of much current interest.<sup>17–29</sup> The most simple carbene, methylene, is a ground-state triplet

with a singlet-triplet splitting (S/T) of 9.05 kcal/mol.<sup>30</sup> The singlet state of carbenes with its empty p orbital is isoelectronic with carbocations and is stabilized more by hyperconjugation than the triplet state which has a singly occupied p orbital. As a consequence, the S/T separation in simple alkyl- and dialkylcarbenes is considerably smaller than the 9.05 kcal/mol found for methylene.<sup>23,28,29</sup> High level *ab initio* calculations yield a S/T splitting of only about 5.2 kcal/mol for methylcarbene<sup>31</sup> and predict dimethylcarbene to have a singlet ground state with a S/T splitting of about 1.5 kcal/mol.<sup>26,28,32</sup>

Alkyl-, dialkyl-, and cycloalkylcarbenes will undergo intramolecular rearrangements.<sup>5–8</sup> A hydrogen or carbon atom

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- (1) (a) The Ohio State University. (b) The University of Georgia.
- (2) Dumas, J. B. *Ann. Chim. Phys.* [2] **1835**, 28.
- (3) Geuther, A. *Liebigs Ann. Chem.* **1862**, 123, 121.
- (4) Hine, J. J. *Am. Chem. Soc.* **1950**, 72, 2438.
- (5) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, 81, 5512.
- (6) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, 82, 1002.
- (7) Hine, J. *Divalent Carbon*; Ronald Press: New York, NY, 1964.
- (8) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964.
- (9) Smith, J. A.; Shechter, H.; Bayless, J.; Friedman, L. *J. Am. Chem. Soc.* **1965**, 87, 659.
- (10) Kaufman, G. M.; Smith, J. A.; Van der Stouw, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1965**, 87, 935.
- (11) Baron, W. J.; DeCamp, M. R.; Henderick, M. E.; Jones, M. J.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Jones, M., Jr., Moss, R., Eds.; Wiley: New York, NY, 1973; Vol. I, p 1.
- (12) Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, NY, 1973; Vol. I, p 153.
- (13) *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, NY, 1975; Vol. II.
- (14) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1975**, 97, 5217.
- (15) Schaefer, H. F. *Acc. Chem. Res.* **1979**, 12, 288.
- (16) Frenking, G.; Schmidt, J. *Tetrahedron* **1984**, 40, 2132.
- (17) Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, 112, 9148.
- (18) Seburg, R. S.; McMahan, R. J. *J. Am. Chem. Soc.* **1992**, 114, 7183.

- (19) Kirmse, W.; Meinert, T.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, 115, 8918.

- (20) Bach, R. D.; Su, M.-D.; Aldabbagh, E.; Andrés, J. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1993**, 115, 10237.

- (21) Storer, J. W.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, 115, 10426.

- (22) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, 93, 1583.

- (23) Khodabandeh, S.; Carter, E. A. *J. Phys. Chem.* **1993**, 97, 4360.

- (24) Platz, M. S.; Modarelli, D. A.; Morgan, S.; White, W. R.; Mullins, M.; Celebi, S.; Toscano, J. P. *Prog. React. Kinet.* **1994**, 19, 93.

- (25) Platz, M. S.; White, W. R.; Modarelli, D. A.; Celebi, S. *Res. Chem. Intermed.* **1994**, 20, 175.

- (26) Richards, C. A. J.; Kim, S.-J.; Yamaguchi, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1995**, 117, 10104.

- (27) Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, 117, 3685.

- (28) Matzinger, S.; Füllscher, M. P. *J. Phys. Chem.* **1995**, 99, 10747.

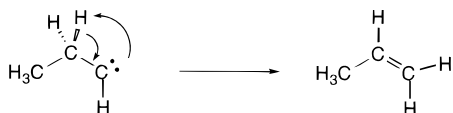
- (29) Sulzbach, H. M.; Bolton, E.; Lenoir, D.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1996**, 118, 9908.

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

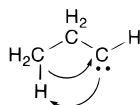
- (31) Gallo, M. M.; Schaefer, H. F. *J. Phys. Chem.* **1992**, 96, 1515.

- (32) Bally, T.; Matzinger, S.; Truttman, L.; Platz, M. S.; Morgan, S. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1964.

## Scheme 1



## Scheme 2



## Scheme 3

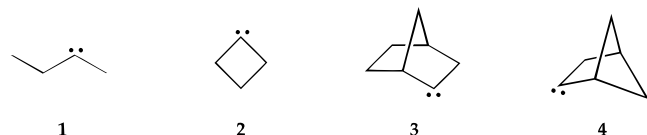


will migrate to the carbenic carbon and restore its electron octet. There are three commonly found rearrangement patterns which are depicted for 1-propylidene. The first is a 1,2-hydrogen shift (Scheme 1) which is predominant in most simple alkyl carbenes with an  $\alpha$ -hydrogen, e.g., dimethylcarbene.<sup>33</sup> This rearrangement has been studied extensively by experiment and by theory.<sup>5–11,15–17,21,28,34</sup>

An alternative is a 1,3-hydrogen shift (Scheme 2) usually found in carbenes with no  $\alpha$ -hydrogens (e.g., *tert*-butylcarbene) and leading to cyclopropanes.<sup>5,8,27,29,35–41</sup>

Instead of a hydrogen, an adjacent carbon can also migrate to the carbenic center (Scheme 3). This rearrangement is particularly important in the case of sterically constrained carbenes, such as cyclobutylidene.<sup>6,9,10,42</sup>

Which migratory process dominates in a particular case is determined by the availability of a suitable migrating group, ground-state orbital alignment, and geometric constraints.<sup>17,34</sup> This prompted us to carry out a theoretical study to elucidate the different behavior of ethylmethylcarbene (EMC, **1**), cyclobutylidene (**2**), 2-norbornylidene (**3**), and 2-bicyclo[2.1.1]hexylidene (**4**).



EMC was chosen because it is a simple unstrained dialkylcarbene. However, it has four distinct possibilities for rearrangement, which are depicted in Figure 1. Rearrangements a–c all involve the migration of a hydrogen atom. The energy difference between a and b gives insight into primary vs secondary hydrogen migration, while the  $\Delta G^\ddagger$  between b and c yields information on 1,2- vs 1,3-migration. Finally, d permits a comparison between carbon and hydrogen migration for the case of unstrained alkylcarbenes.

(33) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034.

(34) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84 and references therein.

(35) Frey, H. M. *Adv. Photochem.* **1964**, *4*, 225.

(36) Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1965**, 3101.

(37) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082.

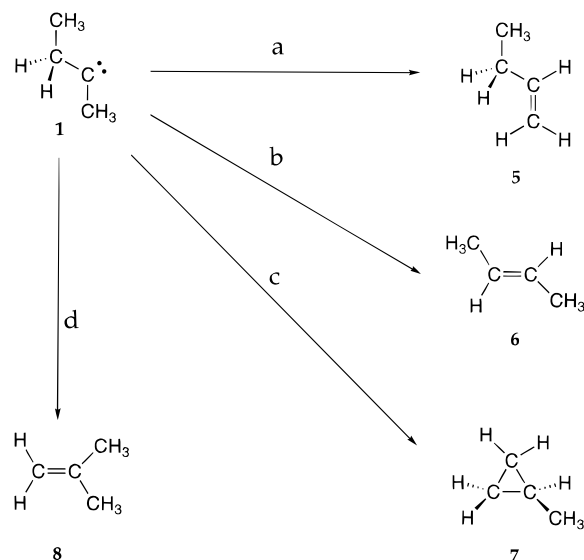
(38) Kirmse, W.; Wedel, W. V. *Ann. Chem.* **1963**, 666, 1.

(39) Friedman, L.; Berge, J. G. *J. Am. Chem. Soc.* **1961**, *83*, 500.

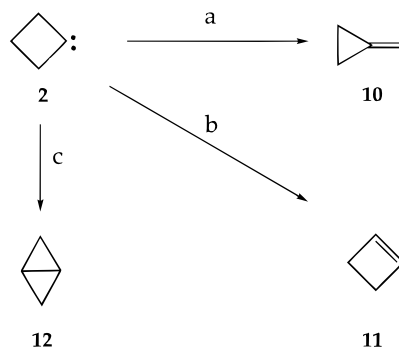
(40) Goldstein, M. J.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 2293.

(41) Fukushima, M.; Jones, M., Jr.; Brinker, U. *Tetrahedron Lett.* **1982**, *23*, 2212.

(42) 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.



**Figure 1.** Possible pathways for rearrangement of ethylmethylcarbene (EMC, **1**): (a) 1,2-H-migration, primary H, (b) 1,2-H-migration, secondary H, (c) 1,3-H-migration, and (d) 1,2-C-migration.



**Figure 2.** Possible pathways for rearrangement of cyclobutylidene, **2**: (a) 1,2-C-migration, (b) 1,2-H-migration, and (c) 1,3-H-migration.

Cyclobutylidene (**2**), 2-norbornylidene (**3**), and 2-bicyclo[2.1.1]hexylidene (**4**) are all examples of strained carbenes. Cyclobutylidene can rearrange in three different ways (Figure 2). We were particularly interested in **2**, because experimentally, C-migration accounts for 85% of the products, 1,2-H-migration for the remaining 15% and 1,3-H-migration is not observed.<sup>6,9,10,42</sup> We hoped to understand the reasons why C-migration becomes the favored path of rearrangement in this case.

2-Norbornylidene (**3**) and 2-bicyclo[2.1.1]hexylidene (**4**) have a very similar carbon framework. This led to the assumption that the stability and rearrangement patterns of **3** and **4** should be similar, too. However, Kirmse *et al.* find a strikingly different behavior. Carbene **3** presumably rearranges into a nortricyclicene, but it can not be trapped with pyridine, implying a lifetime of less than 0.01 ns, if it is indeed formed from its diazirine precursor.<sup>19</sup> Carbene **4** is a trappable intermediate with a lifetime of 50–600 ns (depending on solvent) and rearranges to bicyclo[2.1.1]hex-2-ene.<sup>19</sup> Again, we hoped to understand the reasons for this difference in behavior.

## Methods and Computational Details

All structures in this study were fully optimized if not specified otherwise. In those cases where it was doubtful whether the optimized TS structure connected the reactant carbene with the rearrangement product of interest an intrinsic reaction coordinate following (IRC) was performed. Geometry optimizations that employed second-order Møller–Plesset perturbation theory<sup>43</sup> or density functional theory (DFT)

**Table 1.** Relative Energies (kcal/mol) for Ethylmethylcarbene (**1**)<sup>a</sup> and the Transition States That Lead to 1-Butene (**TS 1–5**), *trans*-2-Butene (**TS 1–6**), *cis*-2-Butene (**TS 1–9**), Methylcyclopropane (**TS 1–7**), and 2-Methylpropene (**TS 1–8**)

level of theory	<b>1</b>	<b>1'</b>	<b>TS 1–5</b>	<b>TS 1–6</b>	<b>TS 1–9</b>	<b>TS 1–7</b>	<b>TS 1–8</b>
BHandHLYP/DZP							
energy relative to <b>1</b>	0.00	1.11	11.48	7.91	8.69	11.00	20.45
with ZPVE correction	0.00	1.75	10.56	6.64	7.43	10.98	20.70
$\Delta G$ rel to <b>1</b>	0.00	1.66	10.67	6.91	7.26	11.71	21.23
MP2/DZP							
energy relative to <b>1</b>	0.00	0.57	6.45	3.28	4.59	4.15	13.22
$\Delta G$ rel to <b>1</b> <sup>b</sup>	0.00	1.13	5.64	2.29	3.15	4.85	14.00
CCSD(T)/DZP							
energy relative to <b>1</b>	0.00	0.73	9.32	6.17	7.34	7.58	17.32
$\Delta G$ rel to <b>1</b> <sup>b</sup>	0.00	1.28	8.51	5.18	5.91	8.28	18.10

<sup>a</sup> **1** denotes the conformer which is stabilized only by C–H hyperconjugation and **1'** is the conformer in which the C–C bond of the ethyl group is aligned with the empty p orbital. <sup>b</sup> BHandHLYP/DZP frequencies and thermal data were employed.

methods<sup>44,45</sup> were carried out with the Gaussian 94 package.<sup>46</sup> For the MP2 calculations the core orbitals and corresponding highest virtual orbitals were kept frozen. The DFT study employed the BHandHLYP functional. BHandH is a hybrid functional in which the exact term for the HF exchange integral has been replaced by a mixture of the HF exchange and a DFT functional. BHandH, which was first introduced in Gaussian92/DFT, is similar to Becke's "half and half" functional.<sup>47</sup> In combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (LYP),<sup>48,49</sup> the hybrid method BHandHLYP is obtained. The ACES II program system<sup>50</sup> was used to optimize the geometries at the CCSD(T) (coupled cluster (CC) with single (S) and double (D) excitations and additional inclusion of perturbative triple excitations) level, because it allows the determination of analytic gradients at this level of theory. Since the  $T_1$  diagnostic yielded values smaller than 0.02 for all structures that were optimized at CCSD(T), a single reference treatment was considered sufficient. The Huzinaga double  $\zeta$  (DZ) C(9s5p/4s2p), H(4s/2s) basis set<sup>51</sup> in Dunning's contraction<sup>52</sup> augmented with a set of five spherical d polarization functions on carbon (orbital exponent  $\alpha_d = 0.75$ ) and a set of three p polarization functions on hydrogen (orbital exponent  $\alpha_p = 0.75$ ) (DZP) was employed for all DFT and MP2 calculations. For the theoretical evaluation at the CCSD(T) level the DZ basis set was augmented with a set of six cartesian d polarization functions on carbon (orbital exponent  $\alpha_d = 0.654$ ) and a set of three p polarization functions on hydrogen (orbital exponent  $\alpha_p = 0.70$ ). To investigate how far the DZP basis set was from the Hartree–Fock limit, HF energy single points for the structures optimized at MP2/DZP and CCSD(T)/DZP were computed for a triple- $\zeta$  C(10s6p/5s3p), H(5s/3s) Huzinaga basis set<sup>51</sup> in Dunning's contraction<sup>53</sup> augmented with diffuse s functions on carbon and hydrogen in addition to two sets of five spherical d polarization functions (orbital exponents  $\alpha_{d1} = 1.50$  and  $\alpha_{d2} = 0.375$ ) and one set of seven f functions (orbital exponent  $\alpha_f = 0.8$ ) on carbon, and two sets of p polarization functions (orbital exponents  $\alpha_{p1} = 1.50$  and  $\alpha_{p2} = 0.375$ ) and one set of five spherical d functions (orbital exponent  $\alpha_d = 1.0$ ) on hydrogen. The latter basis set is designated TZ2P(f,d+). The thermodynamic data were obtained for 1 atm and 298 K.

(43) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(44) Labanowski, J. W.; Andzelm, J. *Density Functional Methods in Chemistry*; Springer: New York, 1991.

(45) Parr, R. G.; Yang, W. *Density Functional Theory in Atoms and Molecules*; Oxford University Press: New York, 1989.

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., *Gaussian 94, Revision C.3*; Gaussian, Inc.: Pittsburgh, PA, 1994.

(47) Becke, A. D. *J. Chem. Phys.* **1992**, *98*, 1372.

(48) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(49) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(50) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem.* **1992**, *S26*, 879.

(51) Huzinaga, S. *J. Chem. Phys.* **1965**, *45*, 1293.

(52) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(53) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

All computations were carried out on IBM 3CT RS6000 workstations at the Center for Computational Quantum Chemistry, the University of Georgia, Athens, GA, Georgia and at the Ohio State University, Columbus, OH.

## Results and Discussion

Intramolecular rearrangements of carbenes proceed via the singlet state,<sup>34</sup> and much of the experimental work on carbenes **1–4** involves initial generation of the singlet from the appropriate precursor. In addition, all of the carbenes considered in this study have a singlet ground state. Hence, we have limited our computational study to the singlet surfaces.

Table 1 summarizes our results for EMC (**1**). The rearrangement to form *trans*-2-butene is energetically most favorable with a barrier of only 5.2 kcal/mol (CCSD(T)/DZP, path b, Figure 1).<sup>54</sup> The barrier for the formation of *cis*-2-butene is 5.9 kcal/mol, only slightly higher than that for the *trans* isomer. The difference is most likely due to repulsion between the two methyl groups which are nearly in plane in the transition state. Formation of 1-butene has a barrier of 8.5 kcal/mol (path a, Figure 1). The transition state for 1,3-H-migration is predicted to be 8.3 kcal/mol (path c, Figure 1), 3.1 kcal/mol higher in energy than the most favorable TS for 1,2-H-migration. At BHandHLYP/DZP, *trans*-butene is 3.1 kcal/mol (298 K, 1 atm) more stable than 1-butene. According to the Bell–Evans–Polanyi principle, the TS that leads to 1-butene should therefore be higher in energy than that for *trans*-butene.<sup>55</sup> With a theoretically derived barrier of 18.1 kcal/mol, C-migration (path d, Figure 1) cannot compete with H-migration in the case of **1**. Hence, the rearrangement product of **1** should contain a mixture of *trans*-2-butene and *cis*-2-butene, but little 1-butene, cyclopropane, or 2-methylpropene. These results are in good agreement with the experimental report of Friedman and Shechter<sup>5</sup> who studied the decomposition of the sodium salt of toluenesulfonyl hydrazones and of Frey and Stevens<sup>36</sup> and Mansoor and Stevens<sup>56</sup> who studied the thermal decomposition of the corresponding diazirine (Table 2). It was noted, however, that photolysis of the diazirine gives a very different product mixture than pyrolysis of nitrogenous precursors (Table 2). Thus, as early as 1965 it was clear that some of the products obtained on photolysis of nitrogenous precursors of carbenes may derive from electronic and vibrationally excited states of the carbene precursor.<sup>35,57,58</sup>

For cyclobutylidene (**2**) a much different energetic ordering is encountered. Table 3 shows that in the case of **2**, C-migration

(54) Storer and Houk (ref 21) find that tunneling effects might further lower the barrier and improve the agreement between experiment and theory.

(55) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11.

(56) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733.

(57) Frey, H. M. *J. Am. Chem. Soc.* **1962**, *84*, 2647.

(58) For a recent review, see: Platz, M. S. *Advances in Carbene Chemistry II*; Brinker, U. Ed.; JAI Press: New York in press.

**Table 2.** Experimental Product Distribution for the Decomposition of Nitrogenous Precursors of Ethylmethylcarbene (**1**)<sup>a</sup>

Precursor	Conditions					
	Δ	67	28	5	0.5	0.0
	hν	38.0	34.7	23.2	3.7	0.3
	Δ	66.6	29.5	3.3	0.5	0.0

<sup>a</sup> See ref 56 and references therein.**Table 3.** Relative Energies (kcal/mol) for the Nonclassical Cyclobutylidene Structure (**2**), the Classical Cyclobutylidene Structure (**2'**), and the Transition States That Lead to Methylene cyclopropane (**TS 2-10**), Cyclobutene (**TS 2-11**), and Bicyclo[1.1.0]butane (**TS 2-12**) at the BHandHLYP/DZP, MP2/DZP and CCSD(T)/DZP Levels of Theory

level of theory	<b>2</b>	<b>2'</b>	<b>TS 2-10</b>	<b>TS 2-11</b>	<b>TS 2-12</b>
BHandHLYP/DZP					
energy relative to <b>2</b>	0.00	0.52	11.93	10.92	16.49
with ZPVE correction	0.25	0.00	11.22	9.12	15.66
Δ <i>G</i> rel to <b>2</b>	0.43	0.00	11.46	9.34	16.07
MP2/DZP					
energy relative to <b>2</b> <sup>a</sup>	0.00		8.75	11.55	14.46
Δ <i>G</i> rel to <b>2</b> <sup>a</sup>	0.00		8.81	10.49	14.55
CCSD(T)/DZP					
energy relative to <b>2</b> <sup>a</sup>	0.00		10.48	10.73	14.52
Δ <i>G</i> rel to <b>2</b> <sup>a</sup>	0.00		10.53	9.67	14.62

<sup>a</sup> BHandHLYP/DZP frequencies and thermal data were employed.

leading to methylenecyclopropane has a Δ*G*<sup>‡</sup> of only 10.5 kcal/mol (CCSD(T)/DZP), about 8 kcal/mol less than the comparable migration for **1**. 1,2-H-migration, on the other hand, has a barrier of 9.7 kcal/mol for **2**, about 4 kcal/mol more than that for **1**. The third possibility, 1,3-H-migration has a Δ*G*<sup>‡</sup> of 14.6 kcal/mol and therefore should not compete with the two aforementioned reactions. This calculated preference for 1,2-H-migration is in slight disagreement with experiment which shows that methylenecyclopropane (via C-migration) is favored over cyclobutene.<sup>6,9,10,42</sup>

As mentioned above, experimental decomposition of nitrogenous precursors of **2** yields a 85:15 mixture of the C migration and the 1,2-H-migration products **10** and **11**.<sup>6,59,60</sup> While MP2/DZP seems to reproduce the experimental results for **2** best, the more sophisticated CCSD(T)/DZP method is in better agreement with the density functional results than with the MP2 values, and CCSD(T)/DZP predicts 1,2-H-migration to be slightly favored over the carbon shift.

To understand these theoretical results, we analyzed the difference between the Hartree–Fock energies and the CCSD(T) energies for the CCSD(T)/DZP geometries and the difference

(59) Brinker, U. H.; Schenker, G. *J. Chem. Soc., Chem. Commun.* **1982**, 679.

(60) The lifetime ( $\tau$ ) of **2** has recently been measured in solution and found to be 4–20 ns in cyclohexane and cyclohexane-*d*<sub>12</sub>, suggesting that  $\tau$  is controlled by unimolecular rearrangements in these solvents. An oxadiazoline precursor was employed. Photolysis of this precursor generated **2** as a species trappable with either pyridine or tetramethylene (TME). It was found that [TME] cannot completely suppress the formation of methylenecyclopropane and cyclobutane and changes the ratio on which these two products are formed. Again the involvement of nitrogenous excited states in product formation is indicated.

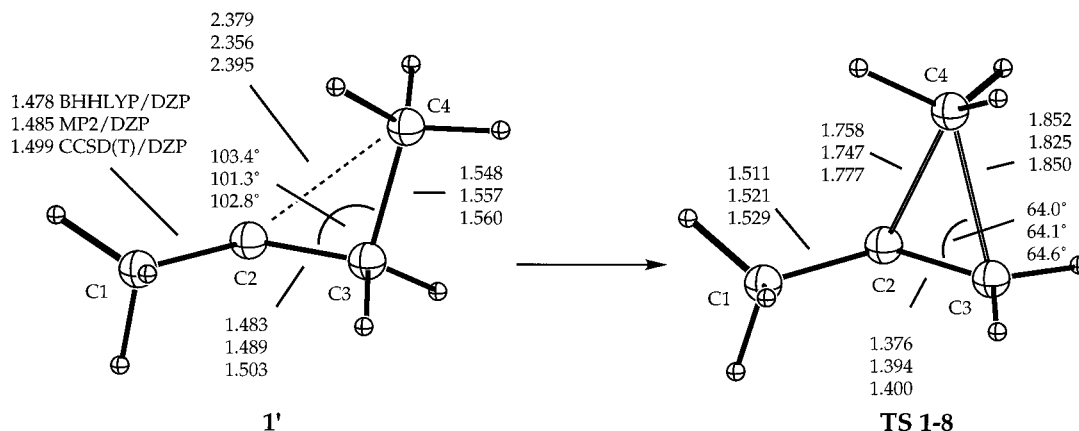
**Table 4.** Effect (kcal/mol) of the Inclusion of Electron Correlation and of an Increase in Basis Set Size on the CCSD(T)/DZP-Optimized and the MP2/DZP-Optimized Geometries of **TS 2-10**, **TS 2-11**, and **TS 2-12** Relative to Cyclobutylidene (**2**)

	CCSD(T)/DZP geometries		MP2/DZP geometries	
	(CCSD(T) – HF)/DZP	TZ2P(fd+) – DZP at HF	(MP2 – HF)/DZP	TZ2P(fd+) – DZP at HF
<b>TS 2-10</b>	6.09	2.16	6.05	1.73
<b>TS 2-11</b>	2.63	0.17	–1.81	–0.64
<b>TS 2-12</b>	6.03	–0.13	2.63	–0.72

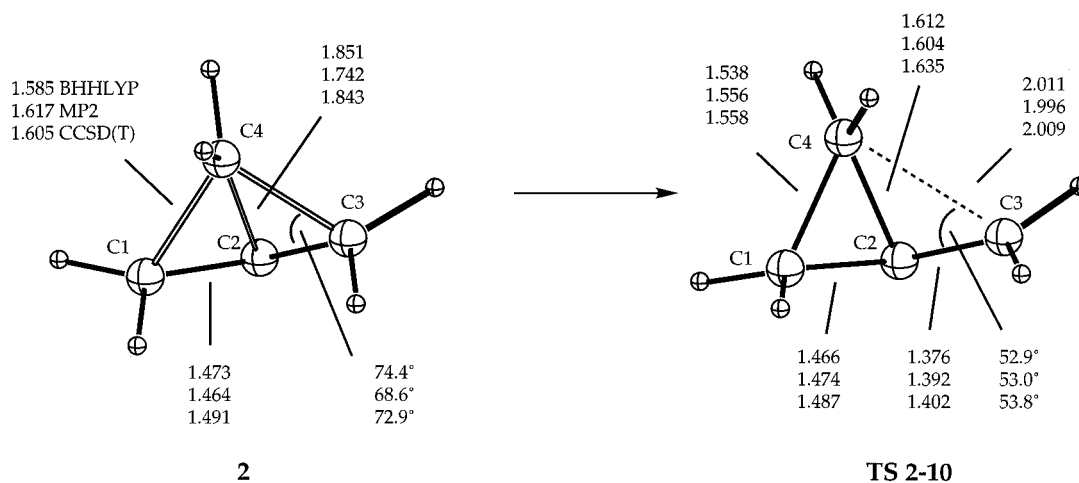
between the HF energies and the MP2 energies for the MP2 geometries. We also compared the HF energies for the DZP basis set with those for a TZ2P(f,d+) basis set which was considered to be close to the HF limit. Table 4, which summarizes our results, shows that at both MP2 and CCSD(T) levels, **TS 2-10** is much more stabilized by electron correlation and an increase in the size of the basis set than either **2** itself or **TS 2-11**. Consequently, a larger basis set in combination with an even more advanced method than CCSD(T) should be able to reproduce the experimental findings without the need to invoke any solvent effect or other intermolecular interaction to explain the results. Since the size of our systems prohibited the use of more advanced levels of theory, we tried to employ Siegbahn's X(PCI-X) scheme<sup>61,62</sup> to estimate what the results would be if the full correlation energy was recovered. However,

(61) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *Chem. Phys. Lett.* **1994**, 223, 35.

(62) Siegbahn, P. E. M.; Svensson, M.; Boussard, P. J. E. *J. Chem. Phys.* **1995**, 102, 5377.



**Figure 3.** Structure of ethylmethylcarbene stabilized by C–C and C–H hyperconjugation (**1'**) and the transition state **TS 1–8** that leads to 2-methylpropene (**8**). All bond lengths are in ångström.



**Figure 4.** Nonclassical structure of cyclobutylidene (**2**) and the transition state **TS 2–10** that leads to methylenecyclopropane (**10**). All bond lengths are in ångström.

the results that we obtained at the MP2 and CCSD(T) levels of theory overestimated the stability of **TS 2–10** and did not lead to a better agreement with the experimental findings. The discouraging results of the X(PCI-X) method may be due to the fact that the geometries in our study change considerably between different levels of theory, so that the assumption of an essentially converged geometry, which is the basis of all single-point calculations and extrapolation schemes cannot be made.<sup>63</sup>

The difference in the height of the activation barrier for C-migration between EMC (**1**) and cyclobutylidene (**2**) may be understood by looking at the structures of the carbenes and of the transition states for C-migration. In **1** (Figure 3) the C–C bond that has to break is 1.56 Å. C<sub>2</sub> and C<sub>4</sub>, between which the new C–C bond is formed, are 2.40 Å apart. Finally, the C<sub>2</sub>–C<sub>3</sub>–C<sub>4</sub> bond angle which is 65° in **TS 1–8** has only been slightly reduced to 103° from the standard value of 109° by hyperconjugation of the C<sub>3</sub>–C<sub>4</sub> bond with the empty p orbital on C<sub>2</sub> in **1**. Consequently **1** has to undergo a large geometrical change before it reaches **TS 1–8**. This is the reason why the  $\Delta G^\ddagger$  for the C migration in **1** is greater than 18 kcal/mol. The situation in **2** is entirely different. The preferred structure for **2** is a nonclassical geometry with a short distance between C<sub>2</sub> and C<sub>4</sub> (Figure 4). This nonclassical structure in which C<sub>4</sub> is pentacoordinate was first described by Schoeller at the MNDO/3 level of theory.<sup>64</sup> This structure can also be viewed as a complex between an allylic  $\pi$ -system and singlet methylene.

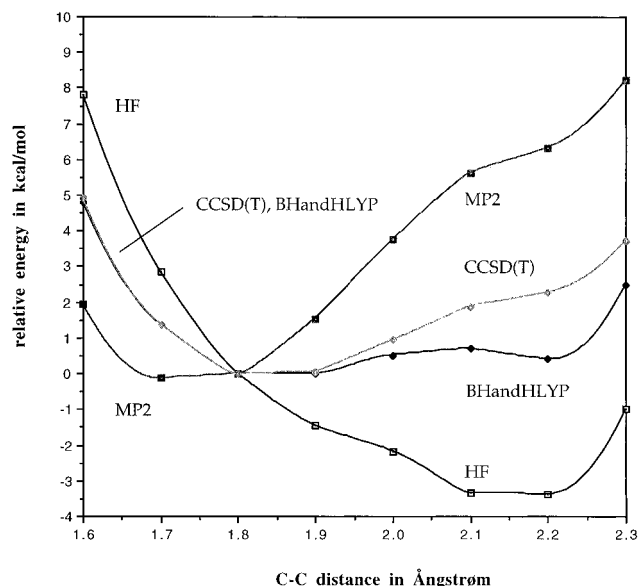
(63) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(64) Schoeller, W. W. *J. Am. Chem. Soc.* **1979**, *101*, 4811.

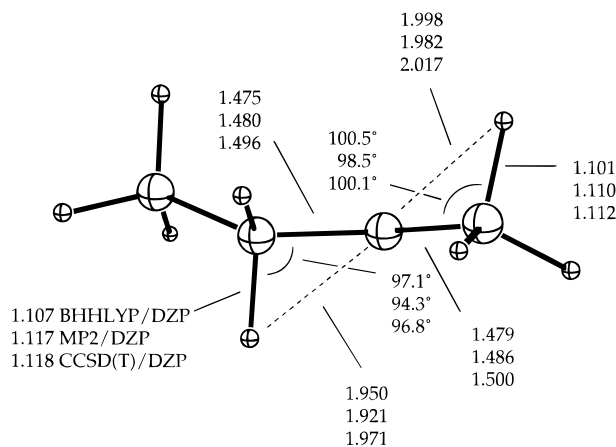
The classical structure is the only minimum at the HF level. It also corresponds to a stationary point at BHandHLYP/DZP, but at this level the nonclassical structure is lower in energy. At MP2/DZP and CCSD(T)/DZP the nonclassical structure is found to be the only minimum. The similarity between the nonclassical structure of **2** and **TS 2–10** (Figure 4) explains the low barrier of only about 10 kcal/mol, since **2** has to undergo only minor geometrical changes to reach **TS 2–10**.<sup>65</sup> It is interesting to note that for **2**, the TS for 1,2-C-migration occurs later along the reaction coordinate than for **1**, because the C–C double bond cannot form as easily as in the acyclic case.

To gain better insight into the relative energy of **2** as a function of the C<sub>2</sub>–C<sub>4</sub> distance and to compare the performance of the MP2/DZP and BHandHLYP/DZP methods relative to CCSD(T)/DZP, we carried out a number of restricted optimizations in which we kept the C<sub>2</sub>–C<sub>4</sub> distance fixed at values between 1.6 and 2.3 Å. This seemed particularly necessary since the density functional method gave two minima, while both MP2 and CCSD(T) yielded only the nonclassical structure as a minimum. Figure 5 shows the change in the relative energies as a function of the C<sub>2</sub>–C<sub>4</sub> distance. While MP2 agrees with CCSD(T) in giving only a single well potential, it greatly overestimates the stability of the nonclassical structure. The overall energy hypersurface at BHandHLYP is in much better agreement with the CCSD(T) results than MP2 is. BHandHLYP/DZP and CCSD(T)/DZP differ only between 2.0 and 2.3 Å. In that region the relative energy at the density functional

(65) A much more detailed discussion based on the molecular orbitals can be found in Schoeller's work (ref 64).



**Figure 5.** Change in the relative energy of cyclobutylidene as a function of the distance between the carbenic carbon  $C_1$  and the carbon on the other side of the four membered ring  $C_3$  at the HF/DZP, MP2/DZP, BHandHLYP/DZP, and CCSD(T)/DZP levels of theory.

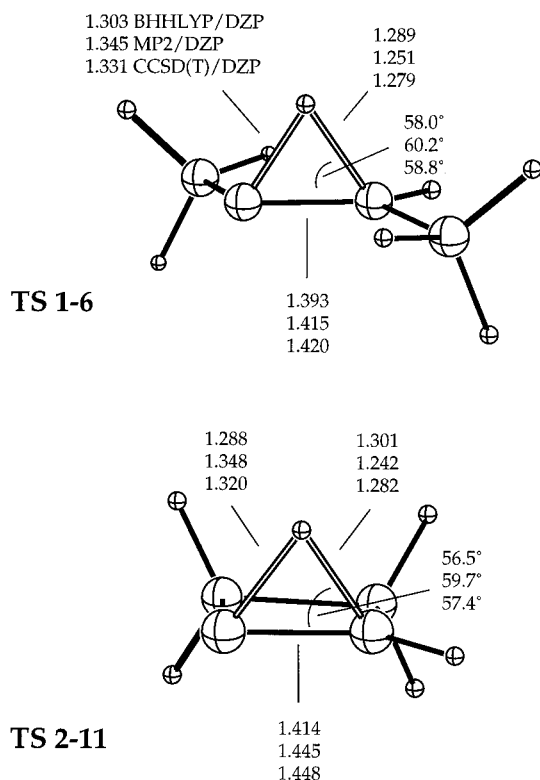


**Figure 6.** Structure of ethylmethylcarbene (**1**) stabilized by hyperconjugation of two C-H bonds. All bond lengths are in Å.

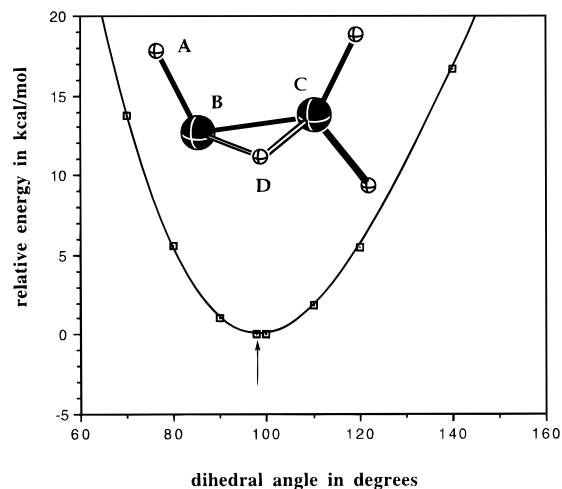
level falls off slightly, giving rise to the shallow well for the classical minimum, while the potential energy at the coupled-cluster level increases slowly.

Figure 6 depicts the lowest energy conformation of **1**. It shows that hyperconjugation of the empty p orbital on the carbenic center with the C-H bond of the methylene group is stronger than that with the C-H bond of the methyl group. This can be seen from the extent by which the donating C-H bonds are elongated as well as from the HCC bond angles with the carbenic carbon ( $97.1^\circ$  vs  $100.5^\circ$ ). Since **1** resembles **TS 1-6** more than **TS 1-5**,  $\Delta G^\ddagger$  for **TS 1-6** is only 5.2 kcal/mol, while **TS 1-5** is 8.5 kcal/mol. From the fact that the TS which leads to *cis*-2-butene is only 0.5 kcal/mol higher in energy than **TS 1-6**, we conclude that the thermodynamic stability of the products is not very important in this case.

To explore the TS geometry preferences, we have examined the barrier for rearrangement in methyl carbene. Figure 8 depicts the change in the barrier height as a function of the H-C-C-H\* angle in methyl carbene (H\* denotes the migrating H). The energy rises sharply as soon as the H-C-C-H\* angle deviates from the ideal value of  $97^\circ$ . A  $20^\circ$  change is sufficient to raise the barrier by about 5 kcal/mol. We conclude that the migrating H and the empty p orbital have to be well aligned in



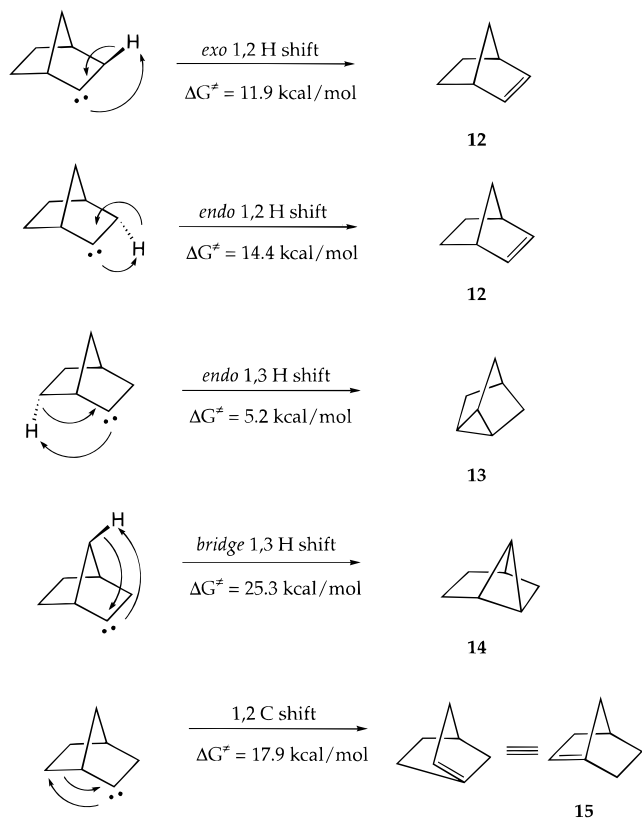
**Figure 7.** Comparison of the lowest energy TS for 1,2-H-migration in ethylmethylcarbene (top) and in cyclobutylidene (bottom). All bond lengths are in Å.



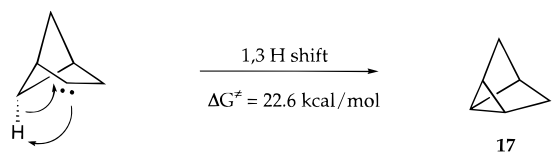
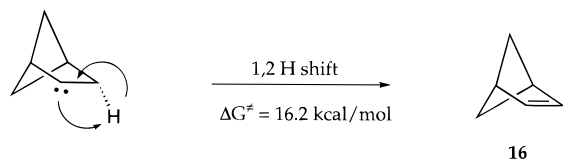
**Figure 8.** Change in the barrier height for 1,2-H-migration as a function of the A-B-C-D dihedral angle in methyl carbene. The arrow denotes the dihedral angle that is found in the nonconstrained transition state.

order to obtain a low energy. The partial formation of the double bond in the TS is another way to rationalize this angle dependence. In the case of **2**, the higher  $\Delta G^\ddagger$  value for the 1,2-H-migration is due to the fact that in order to obtain the aforementioned low-lying TS, the carbon atoms of the four-membered ring are required to all lie in one plane. This causes increased repulsion between the vicinal hydrogen atoms on the two carbon atoms that are not involved in the rearrangement and raises the energy of **TS 2-11** (Figure 7).

The above-discussed BHandHLYP/DZP results were in reasonably good agreement with the CCSD(T)/DZP data for **1** and **2**. Since the last two systems in this study, 2-norbornylidene (**3**) and 2-bicyclo[2.1.1]hexylidene (**4**) are too large to be optimized at the coupled-cluster level, all evaluations for **3** and **4** were only performed at the density functional level. Figures



**Figure 9.** Possible carbene rearrangements of 2-norbornylidene (**3**) with small energetic barriers at the BHandHLYP/DZP level of theory.

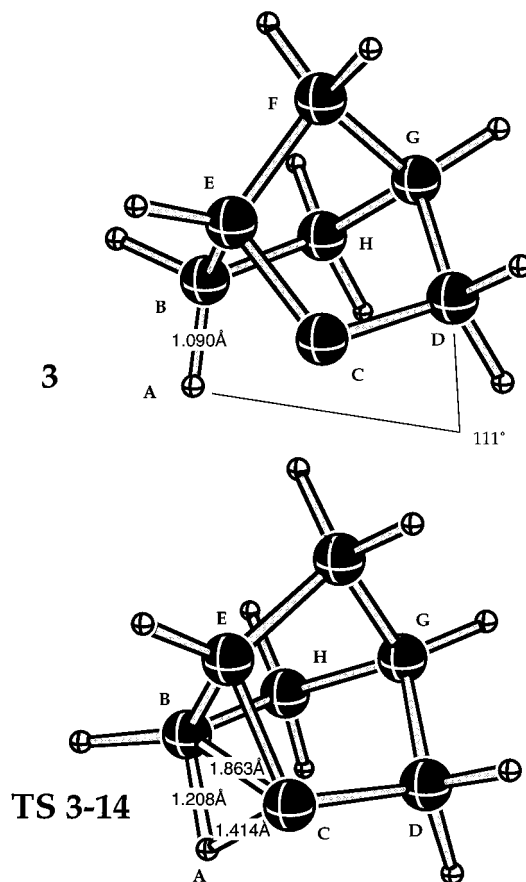


**Figure 10.** Possible carbene rearrangements of 2-bicyclo[2.1.1]-hexylidene (**4**) with small energetic barriers at the BHandHLYP/DZP level of theory.

9 and 10 depict the energetically lowest pathways for rearrangement of **3** and **4** along with their  $\Delta G^\ddagger$  values (1 atm, 298 K) relative to the singlet carbenes.

Our calculations for 2-norbornylidene (**3**) are in accord with the stereoelectronic effect described earlier by Evansck and Houk and numerous experimentalists:<sup>17,34,66</sup> 1,2-H-migration of the *exo*-hydrogen has a barrier of only 11.9 kcal/mol, while the barrier for the *endo*-hydrogen is 14.4 kcal/mol. However, experimental studies have reported nortricyclene (**13**) as the product of the decomposition of the diazirine precursor of **3**, and not norbornene.<sup>5,19</sup> The carbene itself cannot be trapped with pyridine, implying a very short lifetime. In excellent

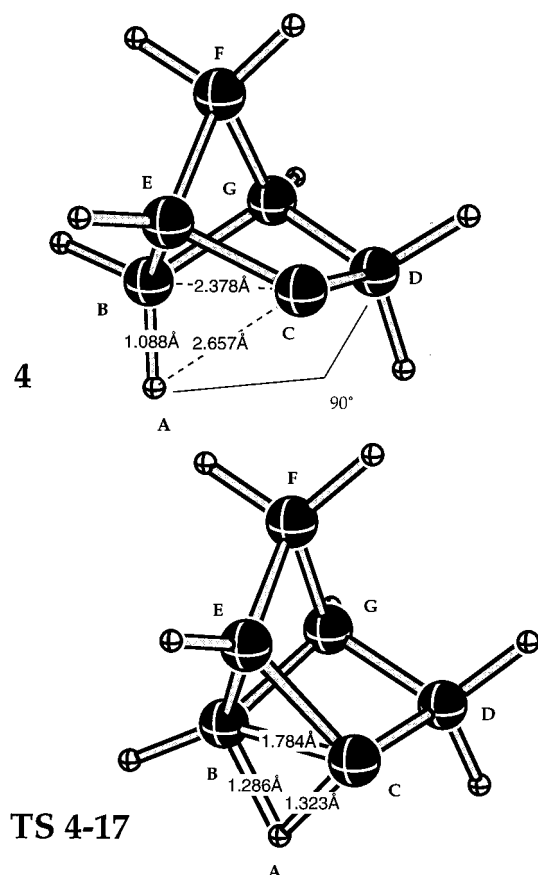
(66) Press, L. S.; Shechter, H. S. *J. Am. Chem. Soc.* **1979**, *102*, 509 and references therein.



**Figure 11.** Singlet 2-norbornylidene (**3**) and the transition state for endo 1,3-H-migration (TS **3-14**) at BHandHLYP/DZP. The A–B–C–D angle in **3** is an indicator of the alignment of the empty p orbital and the migrating H atom.

agreement with these results, we predict that **3** has a barrier of only 5.2 kcal/mol for rearrangement to **13** at the BHandHLYP/DZP level. According to the results for **1** and **2**,  $\Delta G^\ddagger$  is overestimated at the density functional level compared to CCSD-(T)/DZP, and the “actual” barrier should be even lower. All other rearrangements require a much higher  $\Delta G^\ddagger$  and should not be observed (Figure 9). For **4** no low energy pathway for rearrangement exists (Figure 10). The most favorable process, 1,2-H-migration, has a barrier of 16.2 kcal/mol. These findings confirm the experimental result that **4** is a relatively stable carbene with a lifetime of 50–600 ns in acetonitrile and pentane respectively.<sup>19</sup>

The completely different behavior between **3** and **4** only becomes apparent upon a comparison of the transition states for 1,3-H-migration for both molecules. Figures 11 and 12 depict 2-norbornylidene (**3**), 2-bicyclo[2.1.1]hexylidene (**4**), and the corresponding transition states for 1,3-H-migration. For **3**, a second 1,3-H-migration that would involve the bridgehead CH<sub>2</sub> to yield **14** is conceivable, but the TS for this process is much higher in energy (Figure 9). In the case of the 1,2-H-migration the energy of the TS goes up sharply if the migrating H and the empty p orbital are not aligned (compare Figure 8) and similar behavior can be expected for 1,3-H-migration. However, this cannot be responsible for the observed difference in activation energies. Both **3** and **4** are more or less ideally set up for 1,3-H-migration. The A–B–C–D dihedral angle is between 90° (**4**) and 111° (**3**). (The ideal value for 1,2-H-migration is about 97°.) The distance between carbons B and C is 2.3–2.4 Å in both cases. Hence, a difference in the transition states themselves has to be the reason. We believe that ring strain causes TS **4-17** to be higher in energy than TS



**Figure 12.** Singlet 2-bicyclo[2.1.1]hexylidene (**4**) and the transition state for 1,3-H-migration (**TS 4-17**) at BHandHLYP/DZP. The A–B–C–D angle in **4** is an indicator of the alignment of the empty p orbital and the migrating H atom.

**3-13.** In **TS 3-13** one three-membered ring and three five-membered rings are formed during the rearrangement. Figure 11 shows that none of these are very strained. In **TS 4-17** the ring system that is formed contains one three-membered ring, two four-membered rings, and one five-membered ring, while **4** itself consists only of one four-membered ring and two five-membered rings. Figure 12 shows that the new carbon–carbon bond that is formed during the rearrangement forces **TS 4-17**

to resemble tricyclo[2.1.1.0<sup>2,5</sup>]hexane (**17**) more than **4**. As a consequence a sizable fraction of the additional ring strain that is caused by formation of the highly strained **17** will be incorporated in  $\Delta G^\ddagger$  of **TS 4-17**, thereby making it much less favorable than **TS 3-13**.

## Conclusions

In simple acyclic dialkyl carbenes the 1,2-H-migration pathway is the preferred intramolecular reaction, with a  $\Delta G^\ddagger$  of about 5 kcal/mol. Tunneling effects, which were not explored in this study, might give rise to a rate of reaction that corresponds to an even lower barrier.<sup>21</sup> If the carbene can rearrange to yield either a primary or a secondary alkene, the TS for formation of the secondary alkene will be favored by about 3 kcal/mol. 1,3-H-migration has a barrier that is slightly higher than that of 1,2-H-migration and should only be observed in cases where the carbon possesses no  $\alpha$ -hydrogens or the geometry of the carbene favors this rearrangement. For cyclic carbenes, the situation is more complex. Generally, 1,2-H-migration for cyclic carbenes is higher in energy than for the acyclic case due to a rigid carbon framework which does not always allow the ideal orientation of the migrating H, and also due to the formation of a double bond in a ring. For cyclobutylidene (**2**) the similarity between the geometry of the carbene and that of the TS for C migration lowers the barrier for the C migration. A similar situation is encountered for 2-norbornylidene (**3**) where the structure of the carbene favors 1,3-H-migration. Bicyclo[2.1.1]hexylidene (**4**) shows that the structure of the carbene is not the only factor and the barrier to a specific rearrangement may be strongly affected by the product that is generated. The theoretically derived activation energies (at all levels) are in reasonable agreement with the experimental product distributions.

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**Supporting Information Available:** Tables with absolute energies for all minima and transition states (4 pages). See any current masthead for ordering and Internet access instructions.

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