# Formation of Anti-Bredt Olefins from Bridgehead Carbene Precursors: A Computational Study

**C. Michael Geise and Christopher M. Hadad***

*Contribution from the Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210*

*Received January 26, 2000*

**Abstract:** Density functional theory (DFT) calculations are employed to examine the energetics of the rearrangement of bridgehead carbenes to anti-Bredt olefins. These C-migrations are found to have very small activation barriers. For instance, rearrangement of bicyclo[2.2.2]octylcarbene has a transition-state energy that lies 3.8 kcal/mol above the carbene. These rearrangements are also quite exothermic, despite the instability of the bridgehead alkene. Rearrangement of bicyclo[1.1.1]pentylcarbene to bicyclo[2.1.1]hex-1-ene is exothermic by 18.4 kcal/mol. The greater thermodynamic stability of the anti-Bredt olefin products, as well as the low reaction barrier, demonstrates that bridgehead carbenes are a viable source of these strained alkenes.

## Introduction

The study of strained organic molecules has fascinated physical organic chemists for over a century. One of the best-known classes of highly strained reactive organic molecules is bicyclic hydrocarbons which contain a bridgehead double bond. Since Bredt noted in 1924[1] that pinane and camphane systems tend to avoid bridgehead double bonds, these molecules have become a focus for many synthetic and physical organic chemists.[2,3] However, despite the early interest in this class of molecules, a practical preparation of these molecules remained elusive for many years.

One promising idea that gained early popularity was the possibility of making bridgehead olefins from carbenes.[4] Given the propensity for C–C bond insertion by the unsaturated carbene center, it was proposed that either carbene precursors could provide an entry into bridgehead alkenes, or conversely, bridgehead alkenes, being highly strained molecules, could provide an entry into the synthesis of carbenes. Indeed, Jones, Platz, and co-workers have shown experimentally that homocub-9-ylidene (**A**) is in equilibrium with homocub-1(9)-ene (**B**) and the equilibrium constant is near unity at 20 °C.[3d] Calculations by Hrovat and Borden have supported the relative energies of the carbene to bridgehead alkene conversion.[3e,f]



**A**          **B**
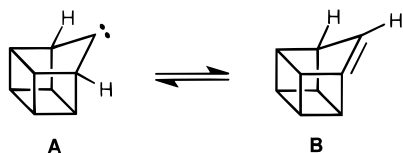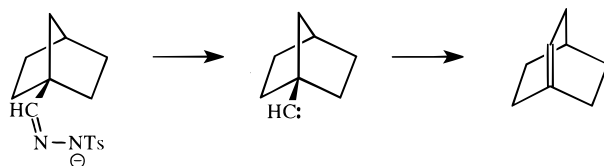
## Scheme 1



Early work on C-migrations in bridgehead carbenes by Wilt[5] involved the generation of 1-methylidenebicyclo[2.2.1]heptane from the thermal decomposition of the tosyl hydrazone salt precursor (Scheme 1). The carbene was not isolated, but products consistent with a carbene intermediate were observed. The example of 1-methylidenebicyclo[2.2.1]heptane and its rearrangement raise an interesting question. Is there a preference for expansion into the 1- or 2-carbon bridge? Experimental evidence shows that, in this case, insertion into the 1-bridge dominates.[4,6] However, as these experiments involved the use of nitrogenous precursors, the degree of participation of the free carbene as compared to the excited states of the precursor is uncertain although rearrangements upon thermolysis are less frequent than upon photolysis.[7] The expansion into the 1-carbon bridge is an interesting result, as the carbene rearrangement is under kinetic control and gives the less stable bridgehead olefin. This behavior is similar to that observed in bridgehead carbocations.[8]

* Address correspondence to this author. E-mail: hadad.1@osu.edu.
(1) Bredt, J.; Thouet, H.; Schmitz, J. *Liebigs Ann. Chem.* **1924**, 437, 1.
(2) Maier, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.
(3) (a) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067. (b) Luef, W.; Keese, R. *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1991; Vol. 20, p 231. (c) Szeimies, G. *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press: Stamford, CT, 1998. (d) Chen, N.; Jones, M., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981. (e) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2719. (f) Hrovat, D. A.; Borden, W. T. *Mol. Phys.* **1997**, *91*, 891.
(4) See: Jones, M. *Advances in Carbene Chemistry*; JAI Press: Stamford, CT, 1998; Vol. 2, p 79.

(5) Wilt, J. W.; Schneider, C. A.; Dabek, H. F., Jr.; Kraemer, J. F. *J. Org. Chem.* **1966**, *31*, 1543.
(6) (a) Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8209. (b) Ruck, R. T.; Jones, M., Jr. *Tetrahedron Lett.* **1998**, *39*, 4433.
(7) (a) Modarelli, D. A.; Morgan, S. C.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034. (b) White, W. R.; Platz, M. S. *J. Org. Chem.* **1992**, *57*, 2841. (c) Celibi, S.; Leyva, S.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8613. (d) Moss, R. A.; Ho, G.-J. *J. Phys. Org. Chem.* **1993**, *6*, 126. (e) Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072. (f) Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183. (g) Yamamoto, N.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Wilsey, S. *J. Am. Chem. Soc.* **1994**, *116*, 2064. (h) Fox, J. M.; Scacheri, J. E. G.; Jones, K. G. L.; Jones, M., Jr.; Shevlin, P. B.; Armstrong, B.; Sztyrbicka, R. *Tetrahedron Lett.* **1992**, 33, 5021. (i) Bonneau, R.; Liu, M. T. H. *Advances in Carbene Chemistry*; JAI Press: Stamford, CT, 1998; Vol. 2, p 1. (j) Platz, M. S. *Advances in Carbene Chemistry*; JAI Press: Stamford, CT, 1998; Vol. 2, p 133.

**Table 1.** Relative Energies and Selected Bond Lengths and Angles for All Stationary Points at the B3LYP/6-31G* Level[a]

| species | descriptor | $\Delta H_0$ | $\Delta H_{298}$ | $\Delta G_{298}$ | $r$ | $\alpha$ |
|---|---|---|---|---|---|---|
| **1** | 1[1.1.1](1) | 0.0 | 0.0 | 0.0 | 1.732 | 82.3 |
| **TS1−1P** | | −0.1 | −0.6 | −0.5 | 1.760 | 78.0 |
| **1P** | | −18.4 | −18.8 | −17.8 | | |
| **2a** | 1[2.1.1](2) | 0.0 | 0.0 | 0.0 | 1.663 | 93.2 |
| **TS2a-2aP** | | 1.9 | 1.6 | 2.2 | 1.840 | 73.2 |
| **2aP** | | −40.6 | −41.0 | −40.3 | | |
| **2b** | 1[2.1.1](1) | 0.0 | 0.0 | 0.0 | 1.676 | 87.0 |
| **TS2b-2bP** | | 2.1 | 1.7 | 2.4 | 1.864 | 63.1 |
| **2bP** | | −5.8 | −6.0 | −5.6 | | |
| **2c** | 2[2.1.1](1) | 0.0 | 0.0 | 0.0 | 1.611 | 99.8 |
| **TS2c-2cP** | | 5.7 | 5.4 | 6.0 | 1.869 | 70.3 |
| **2cP** | | −36.4 | −36.7 | −36.0 | | |
| **3a** | 2[2.2.1](2) | 0.0 | 0.0 | 0.0 | 1.621 | 94.8 |
| **TS3a-3aP** | | 7.4 | 7.2 | 6.9 | 1.904 | 69.2 |
| **3aP** | | −53.0 | −53.3 | −52.6 | | |
| **3b** | 2[2.2.1](1) | 0.0 | 0.0 | 0.0 | 1.629 | 92.3 |
| **TS3b-3bP** | | 3.5 | 3.1 | 3.0 | 1.868 | 68.2 |
| **3bP** | | −32.2 | −32.6 | −31.7 | | |
| **3c** | 1[2.2.1](2) | 0.0 | 0.0 | 0.0 | 1.622 | 95.7 |
| **TS3c-3cP** | | 4.4 | 4.0 | 4.7 | 1.849 | 70.6 |
| **3cP** | | −31.3 | −31.6 | −30.9 | | |
| **4** | 2[2.2.2](2) | 0.0 | 0.0 | 0.0 | 1.619 | 90.9 |
| **TS4−4P** | | 3.8 | 3.4 | 4.2 | 1.844 | 68.0 |
| **4P** | | −52.4 | −52.7 | −52.1 | | |

[a] See Scheme 2 for the definition of $r$ and $\alpha$. $\Delta H_0$, $\Delta H_{298}$, and $\Delta G_{298}$ refer to the enthalpy at 0 K, the enthalpy at 298 K, and the free energy at 298 K, respectively. All energies of stationary points within a set of reactant, transition state, and product are relative to the reactant as 0.0 kcal/mol. All energies are in kcal/mol, distances are in Å, and bond angles are in deg.

In this work, density functional theory (DFT) calculations will be used to attempt to answer the following questions. Does the equilibrium lie on the side of the olefin or the carbene? Can DFT methods be used to explain the preference for formation of the less stable anti-Bredt olefin in the case of bicyclo[2.2.2]oct-1-ene due to insertion into the 1-carbon bridge? Density functional theory has been shown to be a dependable method for calculating the rearrangement surfaces associated with singlet carbenes, and should supply some insight into these issues.[9]

## Computational Methods

Geometries of all stationary points were optimized using analytical energy gradients of density functional theory.[10] For these computations, Becke's three-parameter exchange functional[11] (B3) with the nonlocal gradient correlation functional of Lee−Yang−Parr[12] (LYP) was used. The calculations were carried out with the Gaussian 98 suite.[13] All stationary points were optimized using the 6-31G* basis set,[14] and each was confirmed to be a transition state or a minimum by a vibrational frequency calculation. The zero-point vibrational energy (ZPE) correction was scaled by 0.9806.[15] The imaginary vibrational frequency for each transition state was followed after a 10% displacement along the vibrational mode and with a careful optimization (opt = calcfc or opt = calcall) to confirm the connection of each transition state to the corresponding reactant and product.

Single-point energies with a more extended basis set were also performed at the B3LYP/6-31+G** level for all structures. For



**Figure 1.** Three possible rotameric forms of the bridgehead carbenes of 5-methylidenebicyclo[2.2.1]heptane as well as the C−C bond insertion transition states and resulting anti-Bredt olefins. Ring hydrogens have been omitted for clarity and the carbon centers for the migration have been shaded in gray.

**Scheme 2**



stationary points derived from **1** and **2**, CCSD(T)/6-31+G** single-point energies were also evaluated for comparison to the B3LYP values; however, due to the size of the calculation, the CCSD(T) energies were not completed for **3** and **4**.

## Results and Discussion

We have calculated the energies of various bridgehead carbenes, as well as the transition states and bridgehead alkenes originating from C-migration in the [1.1.1] (**1**), [2.1.1] (**2**), [2.2.1] (**3**), and [2.2.2] (**4**) ring systems. The relative energies from the B3LYP/6-31G* calculations are listed in Table 1 for these different ring systems. Due to the different possible rotameric forms, we will attempt to explain our naming system (Scheme 2). Figure 1 shows bicyclo[2.1.1]hexylcarbene in its three rotameric forms (ring hydrogens have been omitted for clarity). Here, **2a** has the empty p orbital of the carbene conjugated to the C−C bond of the 1-carbon bridge, and the H of the carbene is located on the side of the 2-carbon bridge. In Table 1, this is denoted as 1[2.1.1](2). In the general form

(8) Fort, R. C., Jr. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1973; Vol. IV, p 1783.

(9) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F.; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682 and references therein.

(10) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Labanowski, J. W.; Andzelm, J. *Density Functional Methods in Chemistry*; Springer: New York, 1991.

(11) (a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

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

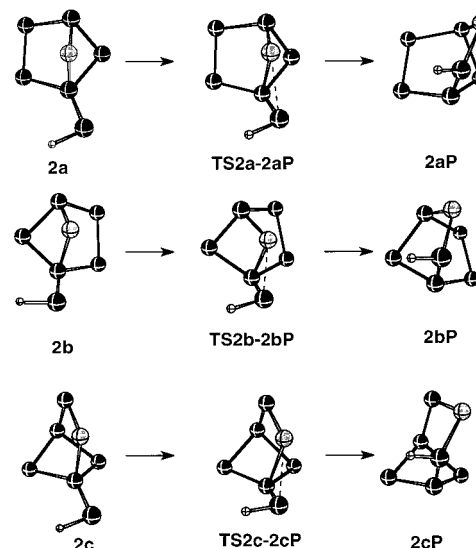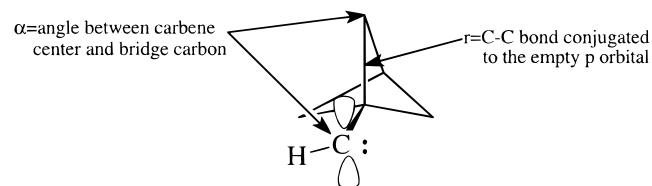(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.6, Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, 28, 213.

(15) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

**Table 2.** Relative Energies of the [1.1.1] and [2.1.1] Stationary Points with the 6-31+G** Basis Set[a]

| species | descriptor | HF | MP2 | MP3 | MP4SDQ | CCSD | CCSD(T) | B3LYP | B3LYP/6-31G* [b] |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 1[1.1.1](1) | 0.0 | 0.0 | 0. | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| **TS1−1P** | | 0.8 | −0.4 | 0.0 | 0.2 | 0.2 | 0.1 | 0.0 | 0.0 |
| **1P** | | −5.2 | −23.6 | −21.4 | −21.4 | −22.1 | −26.2 | −18.5 | −19.3 |
| **2a** | 1[2.1.1](2) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| **TS2a-2aP** | | 6.9 | 0.8 | 3.0 | 3.6 | 3.9 | 3.1 | 1.9 | 2.0 |
| **2aP** | | −26.3 | −44.1 | −40.9 | −40.2 | −40.4 | −43.0 | −39.9 | −42.2 |
| **2b** | 1[2.1.1](1) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| **TS2b-2bP** | | 8.3 | 0.9 | 3.6 | 3.9 | 4.1 | 3.2 | 2.2 | 2.1 |
| **2bP** | | 11.6 | −10.6 | −7.3 | −7.2 | −7.9 | −12.9 | −5.9 | −6.6 |
| **2c** | 2[2.1.1](1) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| **TS2c-2cP** | | 15.1 | 4.4 | 8.1 | 8.9 | 9.5 | 8.0 | 5.8 | 5.6 |
| **2cP** | | −18.2 | −40.6 | −35.5 | −34.5 | −34.1 | −37.3 | −35.9 | −38.2 |

[a] All energies of stationary points within a set of reactant, transition state, and product are relative to the reactant as 0.0 kcal/mol, and are at the bottom of the well (they do not include a ZPE correction). The B3LYP/6-31G* optimized geometry was used in each case. [b] Optimized B3LYP/6-31G* energies for comparison.

**Scheme 3**
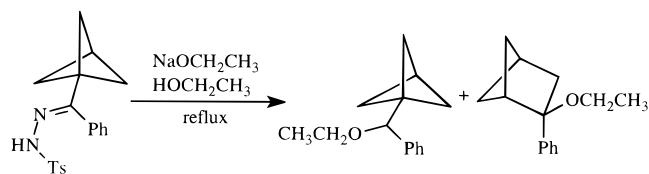


$A[X.Y.Z](B)$, $A$ indicates which bridge of the bicyclic system is conjugated to the carbene p-orbital, $B$ indicates which bridge is syn to the carbene H, and $[X.Y.Z]$ refers to the size of the bicyclic structure. Similarly, **2b** is denoted 1[2.1.1](1) and **2c** is 2[2.1.1](1).

Single-point energy calculations for **1** and **2** with the 6-31+G** basis set (Table 2) using both density functional and coupled cluster levels of theory were used to evaluate the reliability of the density functional theory values. The energies calculated at the B3LYP/6-31G* level (Table 1) are in good agreement with the extended basis set (B3LYP/6-31+G**// B3LYP/6-31G* and CCSD(T)/6-31+G**//B3LYP/6-31G*) calculations (Table 2). The relative energies are all within 3 kcal/ mol (with the exception of bicyclo[2.1.1]hex-1-ene) and the B3LYP method appears to underestimate slightly the barrier heights relative to the CCSD(T) level. More importantly, the relative energy trends are the same at all theoretical levels employed. Therefore, all energies given below will be at the $\Delta H_0$ level from the B3LYP/6-31G* calculations, unless noted otherwise.

**(a) Bicyclo[1.1.1]pentylcarbene.** Experimental evidence suggests that the anti-Bredt olefin product, bicyclo[2.1.1]hex-1-ene (**1P**), can be formed by the decomposition of the appropriate tosylhydrazone formed from bicyclo[1.1.1]pentylphenyl ketone (Scheme 3).[16] The formation of products due to trapping by ethanol is consistent with the intermediacy of a bridgehead carbene but a cationic process may also be possible.

Two major concerns associated with this proposed mechanism are the following: (1) Is the reactive carbene or the highly strained anti-Bredt olefin favored at equilibrium, and (2) does the transition state for rearrangement lie within an accessible energy regime? Since intramolecular rearrangements of carbenes take place in the singlet state,[9,17−20] the calculations included in this study are limited to the singlet surfaces.

The singlet carbene **1** shows significant conjugation of the empty p orbital on C to the adjacent C−C bond of the alkyl

ring. The small bond angle between the carbene C and the methylene C (82.3°) and the near perpendicular dihedral angle for the carbene H to the bridge C (89.2°) indicate this conjugation. The transition state energy ($\Delta H_0$) for rearrangement is −0.1 kcal/mol (including zero-point energy correction), and the rearrangement is very exothermic (−18.4 kcal/mol). In the transition state for insertion into the neighboring C−C bond of the bicyclic system, the angle between the carbene C and the methylene C has contracted 4.3° (82.3° in **1** to 78.0° in **TS1-1P**). Concurrently, there is a lengthening of the bond between the bridgehead C and the methylene C from 1.732 Å in **1** to 1.760 Å in **TS1-1P**. These small deformations of the early transition state are consistent with the small calculated activation barrier. Even with inclusion of thermal corrections calculated by the vibrational frequency analysis at the B3LYP/6-31G* level, the $\Delta H_{298}$ for **TS1-1P** is still lower in energy (−0.6 kcal/ mol) than **1** (Table 1). Inclusion of the thermal Gibb's free energy correction (298 K) yields a relative energy of activation of 0.5 kcal/mol for **TS1-1P**. This rise in energy is consistent with the entropic penalty associated with losing one degree of freedom on going from **1** to **TS1-1P**. The low energetic barrier, as well as the exothermicity of this rearrangement, not only confirms the feasibility of this rearrangement pathway for the bridgehead carbene, but implies that, if formed under the reaction conditions, it would be difficult to stop the carbene from rearranging to the anti-Bredt olefin.

**(b) Bicyclo[2.1.1]hexylcarbene.** There are three possible conformations for the singlet carbene. As illustrated in Figure 1, the carbene can conjugate its empty p orbital to the C−C bond of either the 1- or 2-carbon bridge. Also, when conjugated to the 1-carbon bridge, the carbene H can be on the side of either the one-carbon or the two-carbon bridge.

Rotamer **2b**, which has the carbene conjugated to the 1-carbon bridge and the carbene hydrogen on the side of the other 1-carbon bridge, is the lowest energy structure. This is followed by structure **2a**, in which the carbene is still conjugated to the 1-carbon bridge, but the carbene H is on the side of the 2-carbon bridge. The highest energy structure (**2c**) has the carbene conjugated to the 2-carbon bridge. Structures **2b**, **2a**, and **2c** have relative energies ($\Delta H_0$) of 0.0, 0.9, and 2.0 kcal/mol, respectively, and conjugation to the shorter bridge is favored. This ordering can be ascribed to the degree of hyperconjugation of the carbene to the bridgehead C−C bond. In **2b**, the angle between the carbene C and the bridge C−C bond is 87.0°. Compare this with 93.2° for **2a** and 99.8° for **2c**, and the origin of the energy difference of the rotamers becomes clear.

Investigation into the rearrangement surfaces for these species shows that the thermodynamically and kinetically favored

(16) Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194.
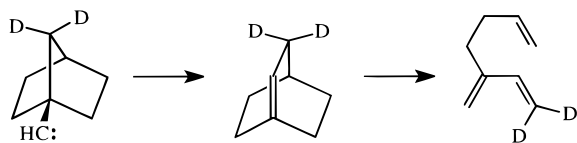(17) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512.
(18) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002.
(19) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964.
(20) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964.

**Scheme 4**



pathway is insertion into the 1-carbon bridge with the hydrogen on the side of the 2-carbon bridge. It is very interesting that the **2aP** product from the rearrangement of **2a** is 34.8 kcal/mol more stable than **2bP** (recall that the initial carbenes **2a** and **2b** differed in energy by only 0.9 kcal/mol). Insertion into the 1-carbon bridge with the hydrogen on the 2-carbon side has an activation barrier of 1.9 kcal/mol, and the reaction is exothermic by 40.6 kcal/mol. This implies that the rearrangement would be very rapid at room temperature. Also, the barrier to insertion into the 1-carbon bridge is 3.8 kcal/mol smaller than insertion into the 2-carbon bridge. Thus, one would expect ring expansion to favor the formation of bicyclo[2.2.1]hept-1-ene rather than bicyclo[3.1.1]hept-1-ene.

The geometric changes from the carbene to the transition state provide some insight into the ordering of their energies. The change in the C−C−C angle on going from **2c** to **TS2c-2cP** is 29.5°, and compares to 23.9° for **2b** to **TS2b-2bP** and 20.0° for **2a** to **TS2a-2aP**. Thus, as formation of **TS2c-2cP** requires larger nuclear deformations from the carbene, it should lie (relatively) higher in energy than either **TS2b-2bP** or **TS2a-2aP**. Although the rearrangement of **2b** is 34.8 kcal/mol less exothermic than the rearrangement of **2a**, it is interesting to note that the transition states are very similar both energetically and geometrically. As mentioned earlier, **2b→TS2b-2bP** has a larger angle deformation than **2a→TS2a-2aP**. There is also a greater lengthening of the (bridgehead) C−(methylene) C bond: 0.187 Å for **2b→TS2b-2bP** compared to 0.177 Å for **2a→TS2a-2aP**. This implies an even later transition state for a much less exothermic process, in agreement with Hammond's postulate.[21] Thus, conjugation to the shorter bridge is more favorable and the small geometric distortion to access the transition state provides an energetic advantage for insertion into the shorter bridge.

Thermal corrections were calculated for each of these species by vibrational frequency analysis. Again, correction to $\Delta H_{298}$ lowers the reaction barrier for rearrangement for all rotamers. Also, upon inclusion of entropy, $\Delta G_{298}$ raises the energy of the transition state structures relative to the carbenes.

**(c) Bicyclo[2.2.1]heptylcarbene.** Experimentally, the rearrangement from 1-methylidenebicyclo[2.2.1]heptane is known to take place preferentially at the 1-carbon bridge by at least an 85:15 ratio relative to the 2-carbon bridge.[4,6] This was determined by labeling experiments associated with the retro-Diels−Alder reaction product (Scheme 4). Jones and co-workers[6b] have also recently investigated the ring-expansion of bicyclo[2.2.1]-heptylcarbene as generated from the photolysis of non-nitrogenous phenanthrene precursors. The carbene can be trapped with alkenes such as tetramethylethylene, and dimeric products are observed when alkenes are not present. These dimeric products dominate the product distribution at room temperature, and at about 100 °C, a retro-Diels−Alder triene was observed as the sole product (Scheme 4). Jones and co-workers have suggested that the presence of the dimeric products at low temperatures is indicative of the formation of the anti-Bredt alkene. On the basis of the low calculated activation

barrier for bridgehead alkene formation (see below), the dominance of the reverse Diels−Alder product at higher temperatures is probably due to a significant activation barrier for the reverse Diels−Alder reaction. The product ratios at different temperatures appear to reflect a transition from a kinetically to a thermodynamically controlled process.

As in the bicyclo[2.1.1]hexane system, the bridgehead carbene of bicyclo[2.2.1]heptane also has three minimum energy conformations. One conformation has the carbene p orbital conjugated to the 1-carbon bridge, **3c**, 1[2.2.1](2). Another structure has the carbene conjugated to a 2-carbon bridge with the hydrogen on the side of the 1-carbon bridge, **3b**, 2[2.2.1](1). And finally, one has the carbene conjugated to the 2-carbon bridge with the hydrogen on the side of the other 2-carbon bridge, **3a**, 2[2.2.1](2). The most stable conformer is **3c**. The relative energies ($\Delta H_0$) of **3c**, **3a**, and **3b** are 0.0, 0.2, and 0.6 kcal/mol, respectively. On the basis of their similar energies, all conformers may be available to the carbene, assuming that the lifetime is long enough to allow equilibration prior to rearrangement.

As expected, insertion into the 2-carbon bridge via **3a** to form the *trans*-alkene **3aP** is thermodynamically favored. It is interesting to note that the *cis*-alkene **3bP** is 21.9 kcal/mol less stable than **3aP.** In fact, insertion via **3c** to give the very unstable **3cP** is energetically comparable to the **3b** path (**3b** is more exothermic by only 0.8 kcal/mol). Kinetically, however, **3a** would be expected to be the slowest reaction, having a transition-state energy of 7.4 kcal/mol, compared to 4.4 and 3.5 kcal/mol for **3c** and **3b,** respectively. Incorporation of thermal corrections from vibrational frequency analyses at the B3LYP/6-31G* level does not change the relative ordering of the transition state energies.

The largest geometric deformation takes place for **3a→TS3a-3aP**. The bridgehead C−bridge C bond length increases by 0.283 Å, compared to 0.237 Å for **3b→TS3b-3bP** and 0.227 Å for **3c→TS3c-3cP**. The largest angle deformation (25.6°) takes place in **3a** (24.1° for **3b** and 25.1° for **3c**). Thus, there is a larger overall geometric change in **3a**, which rationalizes why **TS3a-3aP** should be higher in energy than both **TS3b-3bP** and **TS3c-3cP**. Also, since there is a larger angle contraction in **3c→3cP**, it is expected that this transition state should be higher in energy than **3b→3bP**. As mentioned earlier, the experimental observation is that rearrangement occurs to form **3cP** preferentially. It is not clear what role solvent effects may play in the formation of **3cP** as the major product experimentally. Further investigation would be instrumental in resolving this issue.

**(d) Bicyclo[2.2.2]octylcarbene.** Bicyclo[3.2.2]non-1-ene (**4P**) has been isolated in low-temperature matrixes by the photorearrangement of bicyclo[2.2.2]oct-1-yldiazomethane.[22] This rearrangement surface is similar to those investigated above.

A low barrier (3.6 kcal/mol) to rearrangement is predicted for **4→4P** via transition state **TS4-4P**. This provides a starting point from which one can evaluate whether the photorearrangement takes place by the free carbene or an excited diazo compound.[7,23] It is observed in this case as well that inclusion of thermal corrections from vibrational frequency analyses to give $\Delta G_{298}$ for **4→TS4-4P** raises the energy of the transition state relative to the free carbene. The geometric deformations experienced by this carbene on going to the transition state are also similar to the deformations observed above. The carbene

(21) (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. (b) Leffler, J. E. *Science* **1953**, 117, 340.

(22) Gudipati, M. S.; Radziszewski, J. G.; Kaszynski, P.; Michl, J. *J. Org. Chem.* **1993**, *58*, 3668.
(23) (a) Frey, H. M. *Pure Appl. Chem.* **1964**, *9*, 527 and references therein. (b) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733. (c) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082.

C–bridge C angle contracts 22.9°, and the bridgehead C–bridge C bond length increases by 0.225 Å.

## Conclusions

This study utilizes computational chemistry methods to provide information about some very interesting reaction systems for which only limited experimental information has been obtained. However, some useful information can be extracted. For instance, this study has shown that the equilibria for rearrangement of bridgehead carbenes to anti-Bredt olefins lie heavily on the side of the olefin. Also, the calculated intrinsic barriers to rearrangement are all easily accessible under most reaction conditions, with the largest barrier being 7.4 kcal/mol. In addition, C–C bond insertion for **2a** and **2b** (insertion into the 1-carbon bridge) is predicted to be lower in energy than insertion into the 2-carbon bridge from conformer **2c**. In general, conjugation of the carbene to the shorter bridge is more favorable and the small geometric distortion on traversing the transition state provides an energetic advantage for insertion into the shorter bridge.

These results are also in accord with recent experiments by Tae and Platz[24] for 3-noradamantylcarbene in which ring expansion into the short carbon bridge occurs. (These studies include the reinvestigation and continuation of earlier work by Jones with 3-noradamantyl carbene in which ring expansion to adamantene was deduced from the product distribution.[4]) Furthermore, Tae and Platz observed that the experimentally determined rate of rearrangement of 3-noradamantyl carbene (via a C-migration) is faster than that for adamantyl carbene.[24a] DFT calculations also suggest a very small activation barrier for insertion into the shorter bridge in 3-noradamantyl carbene.[24b]

This work also shows that when various conformations are available to a bridgehead carbene, they are energetically comparable. The calculated barriers for C–C bond insertion of the free carbenes **3b** and **3c** are energetically very similar (for insertion into the 2-carbon and 1-carbon bridge, respectively). It is therefore interesting that a high selectivity should be observed experimentally in the C–C bond insertion process by

the proposed carbene intermediate. This draws into question some of the assumptions made concerning the mechanistic path proposed for the rearrangements, in particular, whether a free carbene is the reactive intermediate involved. An admitted shortcoming[25] of much of the experimental work cited here has been the failure to carry out investigations to clear up such uncertainties. An effort to investigate these systems using non-nitrogenous, and in particular non-diazo precursors, would be very useful. Finally, the homocubylidene–homocubene equilibrium process was also examined as a reference system for our theoretical model. In this case, the equilibrium process is found to be endothermic by ∼9 kcal/mol (favoring the carbene), but gives a transition state energy that lies only 0.4 kcal/mol above the alkene. These results agree with unpublished results at the B3LYP level by Hrovat and Borden.[26] This underestimation of the stability of the alkene is not unreasonable, as the single determinantal B3LYP method would have difficulty describing the twisted alkene, which has been shown to require a 2-configurational wave function for an accurate description.[3f] However, for the bridgehead alkenes discussed above, the alkenes are heavily favored over the carbenes. Therefore, given the magnitude of the exothermicities calculated at present for the systems above, entry from the free carbene to the anti-Bredt olefin will still be an energetically favorable process for these bridgehead carbene systems. An experimental measure of the activation barrier as well as the thermodynamics for these rearrangements would be welcome for comparison to the results reported here.

**Supporting Information Available:** Tables of Cartesian coordinates and vibrational frequencies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA000295G

---

(24) (a) Tae, E. L. Ph.D. Thesis, The Ohio State University, 1999. (b) Zhu, Z.; Platz, M. S. Private communication.

(25) See: Jones, M. *Advances in Carbene Chemistry*; JAI Press: Stamford, CT, 1998; Vol. 2, p 94.

(26) Hrovat, D. A.; Borden, W. T. Unpublished results.