

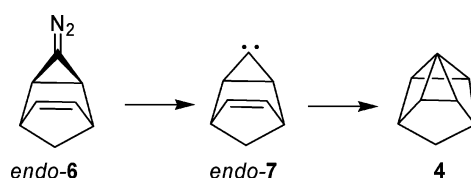
Reactions of *endo*-3-Diazotricyclo[3.2.1.0^{2,4}]oct-6-ene, a Potential Precursor for the Generation of a Neutral C₈H₈ Molecule with a Pyramidally Coordinated Carbon[†]

Jean-Luc Miesusset and Udo H. Brinker*

Institut für Organische Chemie, Universität Wien, Währinger Strasse 38, A-1090 Wien, Austria

udo.brinker@univie.ac.at

Received May 26, 2006



endo-3-Diazotricyclo[3.2.1.0^{2,4}]oct-6-ene (*endo*-**6**) has already been prepared in solution. According to B3LYP/6-311+G(d,p) computations, the corresponding carbene *endo*-**7** easily produces the highly strained neutral C₈H₈ compound **4** comprising a pyramidally tetracoordinated carbon which then rearranges to bridgehead alkene **15** through a cascade of rearrangements. Nonplanar diazocyclopropane structures are predicted for *endo*- and *exo*-**6**. Furthermore, their ring-opened isomers **27** are the first representatives of a new class of non-Kekulé compounds, the diazoallyls.

Introduction

Reactive intermediates¹ are widely used for the construction of highly strained molecules including species comprising a carbon with an inverted coordination geometry.² Among them, a few propellanes² could be isolated. Wiberg also succeeded to record the ¹³C NMR spectra of tricyclo[2.1.0.0^{1,3}]pentane,³ a species bearing a carbon atom with a pyramidal geometry. Theory also supports the existence of systems with (homo) square-pyramidal geometry such as pyramidane,⁴ all-*trans*-fenestrane,⁵ and the hemispiroalkaplanes.⁶ Experimentally, how-

ever, none of these molecules have been generated. Recently, DFT calculations suggested that pentacyclo[4.3.0.0^{2,9}.0^{3,8}.0^{7,9}]-non-4-ene (**1**), a [4.3.4.3]fenestrane,⁷ could be generated from the corresponding cyclopropylidene, tricyclo[3.2.2.0^{2,4}]nona-6,8-dien-3-ylidene (**5**). However, the intermediacy of **1** could not yet be established because only dimerization of **5** was observed.⁸ It will be shown in this paper that **1** is not the only neutral molecule with a pyramidally coordinated carbon that might be experimentally accessible. Indeed, the chemistry of *endo*-3-diazotricyclo[3.2.1.0^{2,4}]oct-6-ene (*endo*-**6**) has already been investigated by Kirmse⁹ who considered the intermediacy of the pyramidally coordinated cation **4**⁺ during the decomposition of *endo*-**6** in methanol. Our results suggest that the reaction products obtained from the reaction of *endo*-**6** under basic conditions are best explained by the participation of intermediate **4**. To corroborate this hypothesis, the rearrangements involving diazo compound **6**, carbene *endo*-**7**, and the corresponding C₈H₉⁺ cations were computed at the B3LYP/6-311+G(d,p) level of theory and compared with each other (Chart 1).

Computational Methods

Gaussian 03¹⁰ was used for density functional theory calculations (DFT) employing Becke's¹¹ three-parameter hybrid method and the

* To whom correspondence should be addressed. Phone: +43-1-4277-52121. Fax: + 43-1-4277-52140.

[†] Carbene Rearrangements 63. For Part 62, see: Miesusset, J.-L.; Brinker, U. H. *J. Org. Chem.* **2005**, *70*, 10572.

(1) *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: Hoboken, 2004.

(2) (a) Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975. (b) Levin, M. D.; Kaszynski, P.; Michl, J. *Chem. Rev.* **2000**, *100*, 169. (c) Dodziuk, H.; Dolgonos, G.; Leszczynski, J. *Tetrahedron* **2003**, *59*, 10013 and references therein.

(3) (a) Wiberg, K. B.; McClusky, J. V. *Tetrahedron Lett.* **1987**, *28*, 5411. (b) Wiberg, K. B.; McMurdie, N.; McClusky, J. V.; Hadad, C. M. *J. Am. Chem. Soc.* **1993**, *115*, 10653. (c) Wiberg, K. B.; Snoonian, J. R. *J. Org. Chem.* **1998**, *63*, 1390.

(4) (a) Minkin, V. I.; Minyaev, R. M.; Zakharov, I. I.; Avdeev, V. I. *Zh. Org. Khim.* **1978**, *14*, 3. (b) Lewars, E. *THEOCHEM* **1998**, *423*, 173. (c) Kenny, J. P.; Krueger, K. M.; Rienstra-Kiracofe, J. C.; Schaefer, H. F., III. *J. Phys. Chem. A* **2001**, *105*, 7745.

(5) (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Schulman, J. M.; Sabio, M. L.; Disch, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 743. (c) Thommen, M.; Keese, R. *Synlett* **1997**, 231.

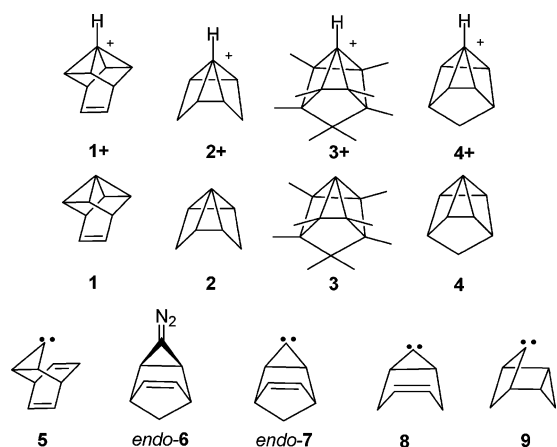
(6) Rasmussen, D. R.; Radom, L. *Chem.–Eur. J.* **2000**, *6*, 2470.

(7) Miesusset, J.-L.; Brinker, U. H. *J. Org. Chem.* **2005**, *70*, 10572.

(8) Huwyler, R.; Li, X.; Bönzli, P.; Neuenschwander, M. *Helv. Chim. Acta* **1999**, *82*, 1242.

(9) Kirmse, W.; Olbricht, T. *Chem. Ber.* **1975**, *108*, 2616.

CHART 1



exchange functional of Lee, Yang, and Parr (B3LYP).¹² Geometries were optimized at the B3LYP/6-31G(d) level of theory, and the stationary points were characterized by vibrational analysis. These geometries were refined at the B3LYP/6-311+G(d,p) level and also confirmed by vibrational analysis. All reported energies include zero-point corrections. If necessary, intrinsic reaction coordinate (IRC)¹³ calculations were performed. Unless otherwise stated, all values refer to B3LYP/6-311+G(d,p) calculations. Atomic charges were calculated using the atomic polar tensor (APT) method¹⁴ and the natural bond orbital analysis¹⁵ (NBO). The APT method is a population analysis based on the calculation of the dipole moment derivatives. The analysis is not distorted by the choice of the basis set. NBO is a method for determining the charge distribution in molecules based on creating atomic natural orbitals. Dashed bonds represent interatomic distances between 164 and 195 pm. Double bonds comprising a full and a dashed line represent distances from 138 to 147 pm.

Results and Discussion

Potential Precursors for Bishomo Square-Pyramidal Species. The molecules **2+**,¹⁶ **3+**,¹⁷ and **4+**¹⁸ represent three bishomo square-pyramidal carbocations¹⁹ which were already observed in superacid solution by NMR spectroscopy.²⁰ As was already proposed by Minyaev²¹ in the early 1980s, it is to be

expected that reactions of the appropriate carbenes also can lead to pyramidal structures such as **2** and **4**.

To our knowledge, tetracyclic hydrocarbon **2** still has not been generated experimentally but only calculated.^{6,21,22} On one hand, bicyclo[4.1.0]hept-3-en-7-ylidene (**8**) as a precursor is not strained enough to complete the intramolecular addition to **2** because our calculations show that **8** is about 15 kcal/mol more stable than **2**. On the other hand, no carbene precursors of strained tricyclo[3.1.1.0^{2,4}]heptan-6-ylidene (**9**) are known and only tricyclo[3.1.1.0^{2,4}]heptan-6-ol derivatives^{16,23} have been prepared.

In contrast, the difference in relative energies of carbene and product is more favorable with **4**, a species for which precursors already have been synthesized.^{9,24,25} Pentacyclooctane **4** was first predicted by Minyaev²¹ to be a local minimum by means of the semiempirical MINDO/3 method and to have a lower heat of formation than tricyclo[3.2.1.0^{2,4}]oct-6-en-3-ylidene (**7**). He also predicted that this system should have a large dipole moment due to the high negative charge on the apical carbon atom. A high kinetic stability (24.6 kcal/mol) was suggested, “making possible the preparative isolation of compound” **4**.²¹ More recently, Radom calculated the proton affinity of **4** at the MP2/6-311+G(2d,p)/MP2/6-31G(d) level of theory and found a high value of 262.0 kcal/mol, much higher than the affinities of pyramidane and proton sponge.⁶ Finally, **4** has been examined by Freeman²² using the B3LYP/6-311+G(3df,2p)/B3LYP/6-31G(d) methodology concerning its potential homoaromaticity, and its properties were compared with those of the corresponding cation **4+**. Freeman found a relatively high negative NICS (nucleus independent chemical shift) value and a positive magnetic susceptibility exaltation, both suggesting homoaromaticity. However, the stabilization energy remained negative.²²

In analogy to the generation of cation **4+** from tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-ol,¹⁸ one could expect that tetracyclo[3.3.0.0^{2,8}.0^{3,6}]oct-4-ylidene (**14**) would be a potential precursor for **4**. Experimentally, **14** was generated from 4,4-dibromotetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane (**13**) with methylolithium in THF.^{24,25} **13** afforded the highly strained homoquadricyclene **15** by the typical cyclobutylidene–alkylidenecyclopropane rearrangement.²⁶ Alkene **15** was trapped either with diphenylisobenzofuran to yield **16** (88%) or with nucleophiles to afford 3-substituted tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octanes **11** and **12** (Scheme 1).²⁴

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
 (12) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
 (13) (a) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.
 (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.
 (14) Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333.
 (15) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.
 (16) Masamune, S.; Sakai, M.; Kemp-Jones, A. V.; Ona, H.; Venot, A.; Nakashima, T. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 769.
 (17) Kemp-Jones, A. V.; Nakamura, N.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1974**, 109.

(18) (a) Hart, H.; Kuzuya, M. *J. Am. Chem. Soc.* **1972**, *94*, 8958. (b) Hart, H.; Kuzuya, M. *J. Am. Chem. Soc.* **1973**, *95*, 4096. (c) Hart, H.; Kuzuya, M. *J. Am. Chem. Soc.* **1974**, *96*, 6436. (d) Hart, H.; Kuzuya, M. *Tetrahedron Lett.* **1973**, 4123.

(19) Prakash, G. K. S.; Rasul, G.; Olah, G. A. *J. Phys. Chem. A* **1998**, *102*, 2579.

(20) Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413.

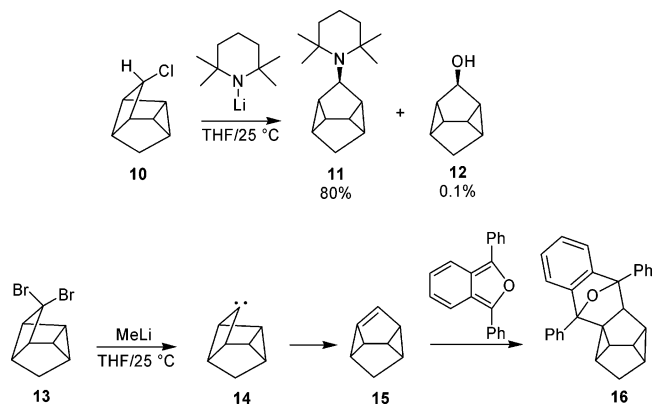
(21) Natanzon, V. I.; Minyaev, R. M. *Theor. Exp. Chem.* **1981**, *17*, 207.
 (22) Freeman, P. K.; Dacres, J. E. *J. Org. Chem.* **2003**, *68*, 1386.

(23) (a) Wiberg, K. B.; Ubersax, R. W. *J. Org. Chem.* **1972**, *37*, 3827.
 (b) Masamune, S.; Vukov, R.; Bennett, M. J.; Purdham, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 8239. (c) Gassman, P. G.; Creary, X. *J. Am. Chem. Soc.* **1973**, *95*, 6852.

(24) Jefford, C. W.; Rossier, J.-C.; Zuber, J. A.; Kennard, O.; Cruse, W. B. *Tetrahedron Lett.* **1983**, *24*, 181.

(25) See also: (a) Stapersma, J.; Kuipers, P.; Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 213. (b) Jefford, C. W.; De los Heros, V. *Tetrahedron Lett.* **1980**, *21*, 913. (c) Jefford, C. W.; De los Heros, V. *Bull. Soc. Chim. Belg.* **1979**, *88*, 969.

(26) Backes, J.; Brinker, U. H. In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E 19b, pp 511–541. For the rearrangement of parent cyclobutylidene(oid) to methylenecyclopropane, see: Brinker, U. H.; Schenker, G. *J. Chem. Soc., Chem. Commun.* **1982**, 679.

SCHEME 1. Generation of Carbene(oid) **14** and Its Further Reactions²⁴

These results are in agreement with our computations at the B3LYP/6-311+G(d,p) level (Figure 1). Cyclobutylidene **14** is 12.3 kcal/mol more stable than its potential reaction product **4** (Figure 2) comprising a bishomo square-pyramidal geometry. In fact, the reaction of **14** to give **4** constitutes a process, which to our knowledge has never been observed experimentally in uncharged molecules. It corresponds to a delocalization of the electrons in the cyclopropane and the two σ bond bridges. The electrons of the divalent carbon do not participate in the delocalization. Carbene **14** exclusively gave **15** by a cyclobutylidene–alkylidenecyclopropane rearrangement.^{24,26} Our calculations suggest that **4** is not produced under the reaction conditions applied.

Isomerization of Carbene *endo*-7. From the calculations, it is obvious that for the generation of **4** it would be better to experimentally start from the isomeric carbene, i.e., *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-3-ylidene (*endo*-7). Because *endo*-7 comprises a cyclopropylidene,²⁷ it could also react under ring opening and form bent allene **18**. Indeed, for this reaction, a very low barrier of 0.3 kcal/mol is predicted at the B3LYP/6-31G(d) level of theory. With the 6-311+G(d,p) basis set, the transition state is even lower in energy than *endo*-7 due to the difference in the zero-point vibrational energies. Such values are in good agreement with results obtained for *cis*-substituted cyclopropylidenes, especially when they are connected to a five-membered ring.²⁸ However, the transformation of *endo*-7 to **4** also occurs almost barrierless with a transition state lying only 0.3 kcal/mol above *endo*-7 (0.1 kcal/mol with 6-31G(d)). Moreover, all attempts to locate an energy minimum for *endo*-7 using MP2/6-311+G(d,p) calculations lead directly to **4** but not to **18**. At the B3LYP/6-311+G(d,p) level of theory, pyramidal **4** is 1.3 kcal/mol more stable than carbene *endo*-7. Furthermore, **4** is more polar than carbene *endo*-7 because a nonbonded electron pair is located^{6,29} on top of the apical carbon of **4**. This is reflected by its large dipole moment of 3.0 D. Accordingly, the relative stability of **4** is enhanced in polar solvents. When the energy in solution given by the polarizable continuum model (PCM)³⁰ is considered for methanol, **4** turns out to be 4.1 kcal/mol more stable than *endo*-7. Additionally, it was also confirmed

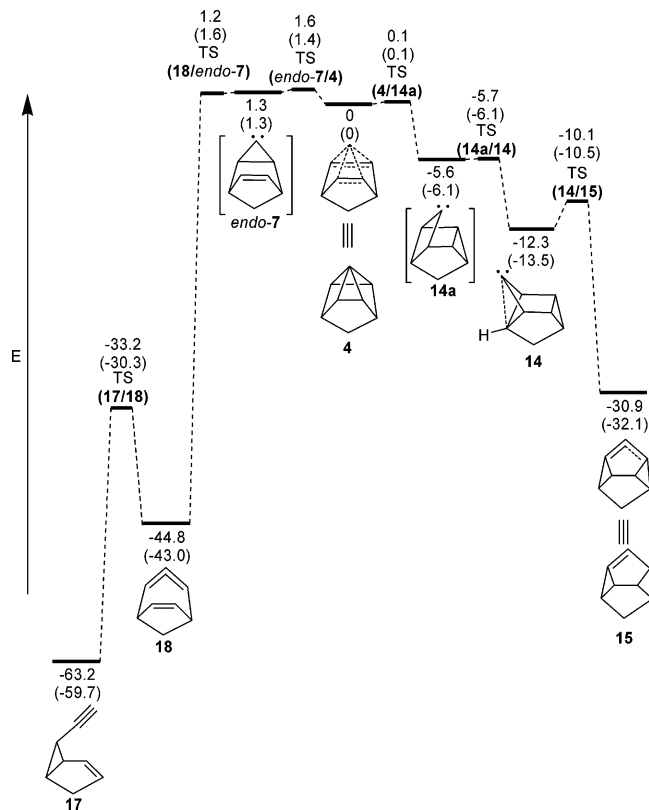


FIGURE 1. Energy diagram showing the conversions of *endo*-7 to **15** and **17**. Relative energies in kcal/mol as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

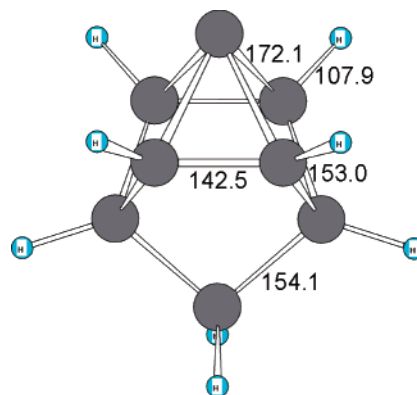


FIGURE 2. B3LYP/6-311+G(d,p) geometry of **4** with selected distances in picometers.

by MP2/6-311+G(d,p) calculations that **4** indeed is a minimum. Bishomo square-pyramidal hydrocarbon **4** easily rearranges under ring opening to cyclobutylidene **14a** which is 5.6 kcal/mol more stable than **4** in the gas phase and 4.3 kcal/mol more stable in methanol. However, **14a** does not exist after zero-point vibrational energy (ZPVE) correction. For **14a**, with -0.12 kcal/mol, the barrier to rearrangement to **14** is calculated to be negative ($+0.03$ kcal/mol without zero-point energies). Carbene **14a** was classified by Freeman as non- to antiaromatic.²² Indeed, in **14a**, the divalent carbon interacts only weakly with the cyclopropane ring. Instead, **14a** is further stabilized³¹ by overlap of the empty 2p orbital (LUMO) of the divalent carbon with the σ orbitals of the two distal C–C bonds (HOMO) of the

(27) Backes, J.; Brinker, U. H. In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E 19b, pp 391–510.

(28) Bettinger, H. F.; Schleyer, P. v. R.; Schreiner, P. R.; Schaefer, H. F., III. *J. Org. Chem.* **1997**, *62*, 9267.

(29) Lewars, E. *THEOCHEM* **2000**, *507*, 165.

(30) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.

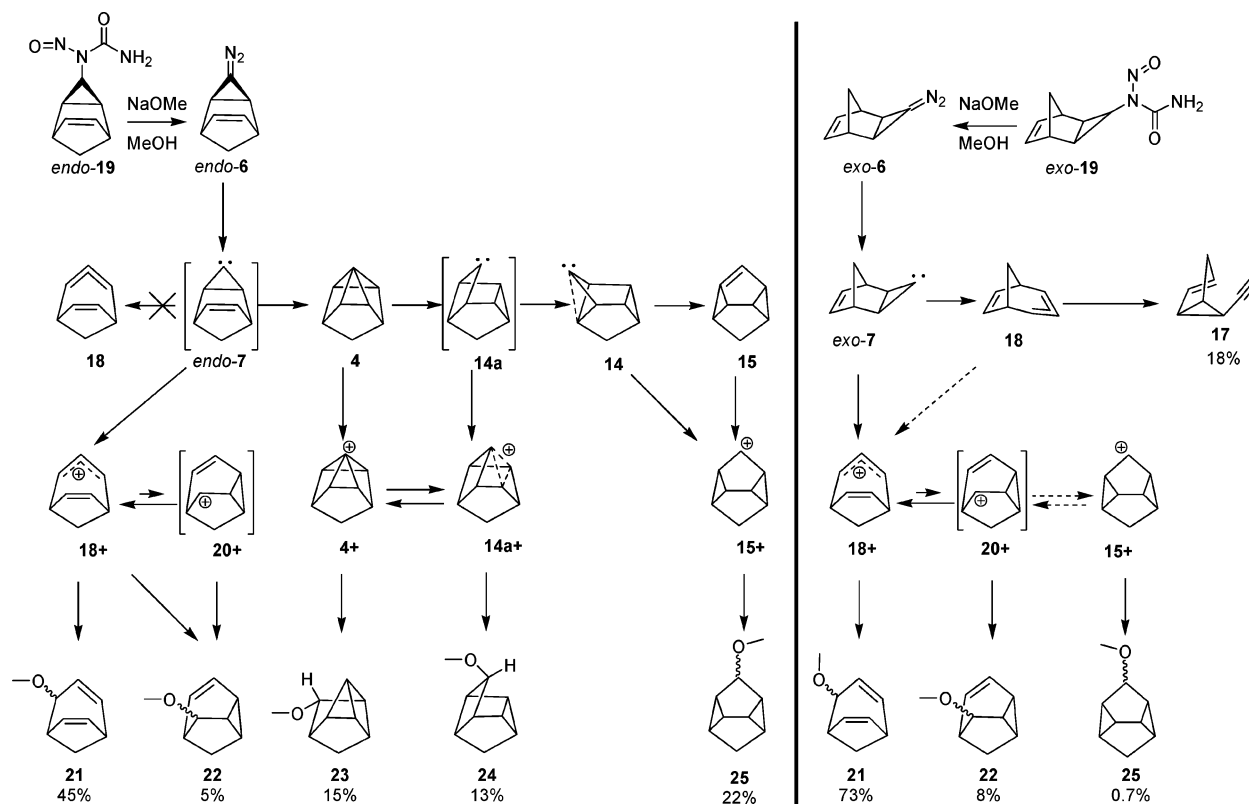


FIGURE 3. Suggested mechanisms based on calculations from this article and experiments for the products resulting from **19** in 2 M NaOMe/MeOH.⁹

cyclobutylidene. Thereby, the lateral bonds of the cyclobutylidene are shortened and the distal bonds are lengthened. This results in the formation of nonclassical cyclobutylidene³¹ **14**, which is 6.7 kcal/mol lower in energy than **14a**. Carbene **14** preferentially rearranges to alkene **15** via a transition state which is only 2.2 kcal/mol higher in energy than **14**.

Experimental Results from the Rearrangements of Carbene 7. These findings correlate well with results obtained experimentally (Figure 3).⁹ When diazo compound *endo-6* was generated from *N*-nitroso(*endo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-3-yl)-urea (*endo-19*) in methanol, a complex product mixture was obtained. Indeed, the products can be thought to derive from the respective reactive intermediates in the **4**, *endo-7*, **14**, and **15** manifold because diazo compounds are known to readily split off N₂ to generate the corresponding carbenes (vide infra). Both methyl ethers **23** and **24** could be formed via species **4** and **14a**, respectively. The most characteristic compounds of this reaction, however, are the 3-methoxytetracyclo[3.3.0.0^{2,8}.0^{4,6}]octanes (**25**). Their formation strongly suggests that **4** rearranges via **14a** to nonclassical cyclobutylidene **14** which undergoes the typical ring contraction to the alkylidenecyclopropane incorporated in **15**. Protonation of **15** affords **15+** which is trapped by methanol. In contrast, **25** is not formed at all from *endo-19* under reaction conditions that generate exclusively carbocations and is formed only in trace amounts by the decomposition of *exo-19*.⁹ In the reaction of *endo-19*, protonation of *endo-7* to some extent should directly lead to the formation of allyl cation

18+ which is trapped by formation of ethers **21** and **22**. These results are to be compared with those obtained from the decomposition of *exo-19*.⁹ In this case, **21** and **22**, the trapping products of **18+**, are the major compounds found (81%). In addition, 18% of *endo-6*-ethynylbicyclo[3.2.1]octa-2,3,6-triene (**17**) is formed, resulting from a rearrangement of bicyclo[3.2.1]octa-

In our opinion, the failure to observe the rearrangement *endo-6* → **17** and the fact that *exo-6* forms almost no **25** are explained best by assuming that *endo-7* almost exclusively rearranges to **4** and not to **18** to prevent the formation of **17**. The two levels of theory used in this study do not agree upon the preferred pathway for the rearrangement in question, i.e., *endo-7* → **4** or *endo-7* → **18**. However, considering the low barriers involved, these observations are best explained with dynamical effects;³⁴ the way the carbene is generated becomes relevant for its further reactions. Because N₂ is preferably split off from the *anti* conformer of *endo-6* (vide infra), the conservation of angular momentum should induce the formation of **4**, following the direct trajectory. Concomitantly, this impedes the rearrangement to allene **18**.

Four mechanisms can be envisaged for the interception of carbenes in NaOMe/MeOH: (a) concerted insertion into the O—H bond or a two-step mechanism, the first step being either

(31) (a) Schoeller, W. W. *J. Am. Chem. Soc.* **1979**, *101*, 4811. (b) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F., III; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682. (c) Stracener, L. L.; Halter, R. J.; McMahon, R. J.; Castro, C.; Karney, W. L. *J. Org. Chem.* **2000**, *65*, 199. (d) Nordvik, T.; Mieusset, J.-L.; Brinker, U. H. *Org. Lett.* **2004**, *6*, 715.

(32) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1981**, *103*, 2874.
 (33) (a) Freeman, P. K.; Pugh, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 2269.
 (b) Freeman, P. K.; Pugh, J. K. *J. Org. Chem.* **2001**, *66*, 5338.
 (34) (a) Carpenter, B. K. *Acc. Chem. Res.* **1992**, *25*, 520. (b) Carpenter, B. K. *Angew. Chem., Int. Ed.* **1998**, *37*, 3340. (c) Carpenter, B. K. *Annu. Rev. Phys. Chem.* **2005**, *56*, 57.

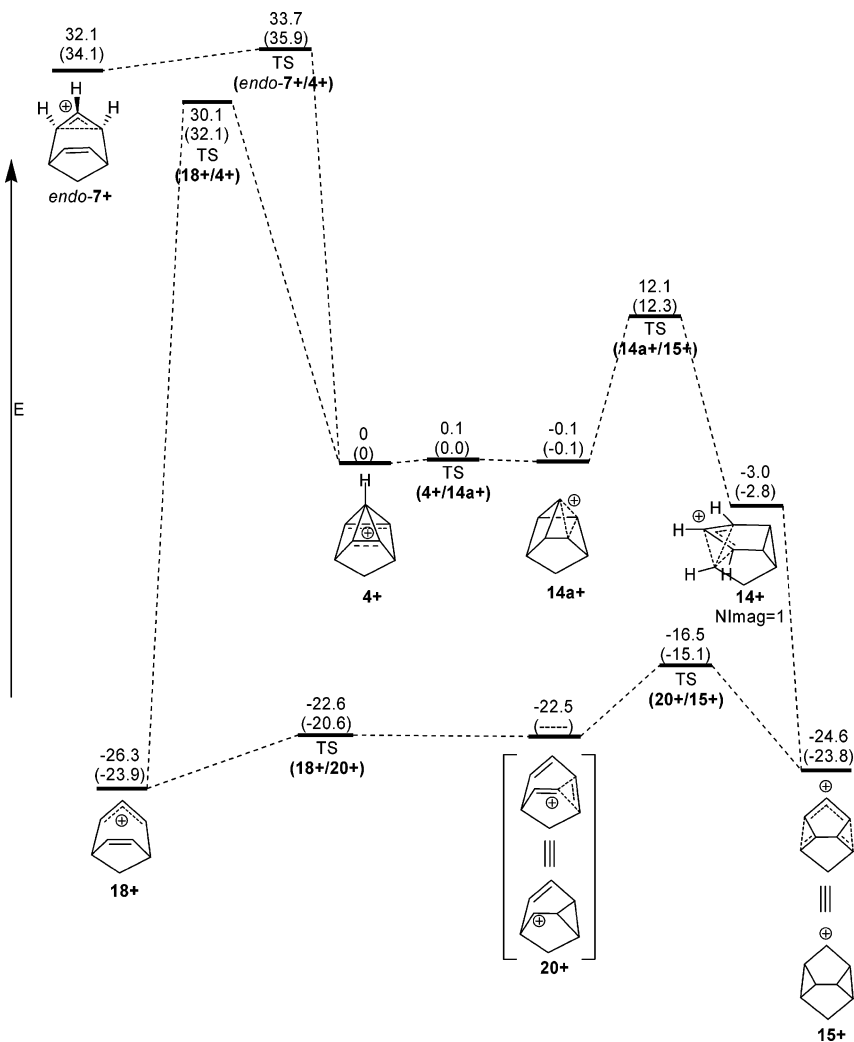


FIGURE 4. Energy diagram showing the relative energies of C₈H₉⁺ cations. Energies in kcal/mol as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

(b) protonation or (c) a nucleophilic attack of methanolate, or (d) an electrophilic addition of the carbene to the oxygen atom of methanol. However, the ylide pathway should not be relevant because alcohols form only weak ylides.³⁵ Formation of a C–O bond by addition of a carbene to a nucleophile is also unlikely because alkoxides prefer to react under C–H insertion.³⁶

Furthermore, in the reaction of *endo*-6, the stereospecific formation of *exo*-24 is a good indication that cyclobutylidenes **14** and **14a** do not react by a direct concerted insertion into the O–H bond of methanol. In particular, a direct insertion of the more stable **14** into the O–H bond of methanol for steric reasons³⁷ should lead to a predominant formation of *endo*-24, a compound which was not isolated from the solvolysis experiments.

Therefore, formation of all methyl ethers preferentially could occur through the corresponding cations. An important question, however, needs to be resolved: can the transient species **4**,

14, **14a**, **15**, and **18** still be protonated³⁸ under the strongly alkaline conditions used for their generation?

Isomerization of the C₈H₉⁺ Cations. To answer this question, the relative energies of the resulting C₈H₉⁺ family of cations (Figure 4) and the proton affinities of the corresponding bases were calculated. The C₈H₉⁺ manifold was already described using the MINDO/3 method,³⁹ and **4+** and **14a+** were further investigated recently at the MP2/6-31G(d)¹⁹ and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)²² levels of theory. Our DFT results are in good agreement with the results obtained previously.³⁹ The most relevant differences pertain to the nature of cations **20+** and **14+**. According to our calculations, **14+** is a transient species rearranging to **15+**, whereas MINDO/3 calculations present **14+** as a discrete intermediate. Similarly, **20+** is found as a minimum only with the 6-311+G(d,p) basis set. However, after consideration of the zero-point energy, the transition state leading to **18+** is lower in energy than **20+**. Moreover, the high energetic cyclopropyl cation *endo*-7+ was found to be a relatively stable intermediate with a barrier of

(35) Kirmse, W. *Eur. J. Org. Chem.* **2005**, 237.

(36) Oku, A.; Harada, T. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier: Amsterdam, 2001; Vol. 3, pp 287–316.

(37) (a) Bobek, M. M.; Brinker, U. H. *J. Am. Chem. Soc.* **2000**, *122*, 7430. (b) Knoll, W.; Bobek, M. M.; Kalchauer, H.; Rosenberg, M. G.; Brinker, U. H. *Org. Lett.* **2003**, *5*, 2943. (c) Kaneno, D.; Tomoda, S. *Org. Lett.* **2003**, *5*, 2947.

(38) Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier: Amsterdam, 2001; Vol. 3, pp 1–52.

(39) Jefford, C. W.; Mareda, J.; Perlberger, J.-C.; Burger, U. *J. Am. Chem. Soc.* **1979**, *101*, 1370.

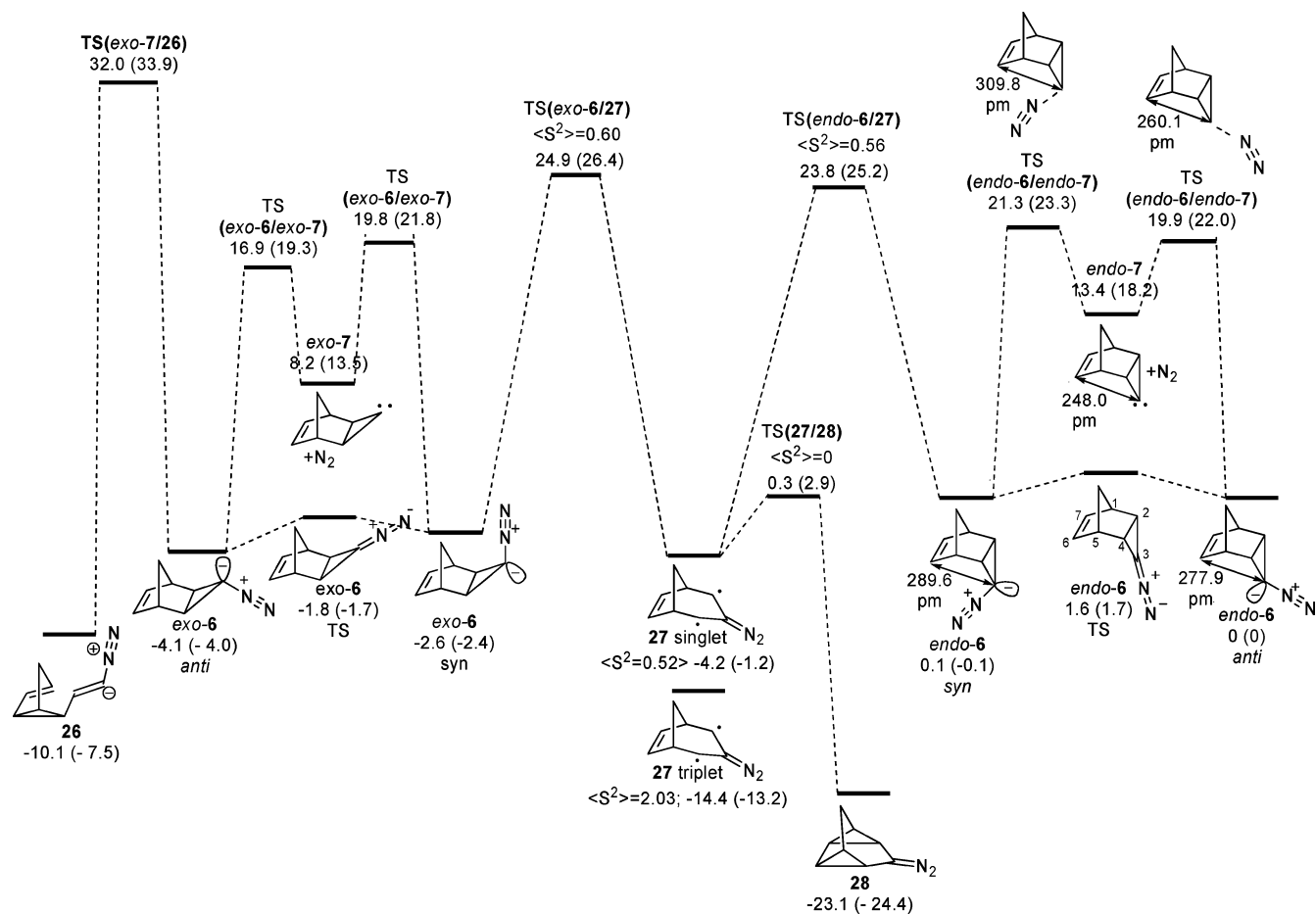


FIGURE 5. Decompositions of **6**. Energies in kcal/mol as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations. **27** and its reactions were investigated using UB3LYP. *Syn* and *anti* describe the position of the diazo group.

1.6 kcal/mol toward rearrangement. The trivalent carbon is strongly pyramidalized, whereas the diametrically opposed C—C bond is elongated (185.2 pm). Consideration of the solvation energy as given by the PCM model for methanol does not alter the energy diagram significantly. The most important effect is obtained by the comparison of the energies of **4+** and **14a+**: the relative stability of **14a+** when compared with **4+** is enhanced by 0.7 kcal/mol. Cations **4+** and **14a+** are in rapid equilibrium and are separated from further rearrangements by relatively high barriers of 12.1 and 30.1 kcal/mol, respectively. Therefore, in methanol, both cations should be trapped efficiently by the solvent to afford **23** and **24**. Interestingly, according to the APT (atomic polar tensor)¹⁴ model, the apical carbon of **4+** is partially negatively charged (−0.378), whereas the same atom in **14a+** has a positive partial charge (+0.018); i.e., this atom switches its charge rapidly and reversibly. When considering proton affinities (PA),⁴⁰ **4** (267.3 kcal/mol with B3LYP/6-311+G(d,p), 262.0 kcal/mol at the MP2/6-311+G(2d,p)/MP2/6-31G(d) level of theory⁶), **14a** (261.5 kcal/mol), but also strained alkene **15** (260.5 kcal/mol), and bicyclic allene **18** (248.2 kcal/mol) all have the ability to be readily protonated, even under the strong basic conditions applied. The proton affinity of **4**, **14a**, and **15** is even higher than the one for 3,4-dimethylthiazolyliidene (252.5 kcal/mol). The pK_a of the con-

jugate acid of 3,4-dimethylthiazolyliidene was estimated to be 16.5 in DMSO⁴¹ and 18.9 in water.⁴² Allene **18** also is more basic than diazo compound *endo-6* (PA = 230.6 kcal/mol). Nonetheless, even under protic conditions, an important fraction of **4**, **7**, **14**, **14a**, and **18** rearranges still as neutral species.

Isomerization of Diazo Compound 16. However, another reaction step still requires more attention: can *endo*- and *exo-6* both really be considered as carbene sources, or do intramolecular rearrangements proceed more easily (Figure 5)?

According to DFT calculations, *endo-6* splits off nitrogen to give carbene *endo-7*. For this process, a barrier of 19.9 kcal/mol needs to be overcome (Figure 5). During the course of the reaction, the distance between C3 and C6 is shortened from 277.9 pm in *endo-6* to 260.1 pm at the transition state (TS) (*endo-6/endo-7*) to 248.0 pm in *endo-7*, favoring the further reaction to **4**. A rearrangement of *endo*- and *exo-6* to 3-diazotetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (**28**)⁹ is not supported by our calculations. A concerted mechanism is unlikely because under thermal conditions [2+2]-cycloadditions are symmetry-forbidden. Instead, a stepwise reaction could happen: singlet diradical **27** is slightly more stable than *endo-6* and rearranges easily to **28** with a barrier of 4.2 kcal/mol. However, our calculations predict a high barrier for the conversion of *endo-6* to **27** (23.8 kcal/mol). It is worth noting that the use of restricted density functional theory for this process leads to a higher energy

(40) For more accurate estimations of basicities, see: (a) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717. (b) Schmidt am Busch, M.; Knapp, E.-W. *ChemPhysChem* **2004**, *5*, 1513.

(41) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1991**, *113*, 985.

(42) Washabaugh, M. W.; Jencks, W. P. *Biochemistry* **1988**, *27*, 5044.

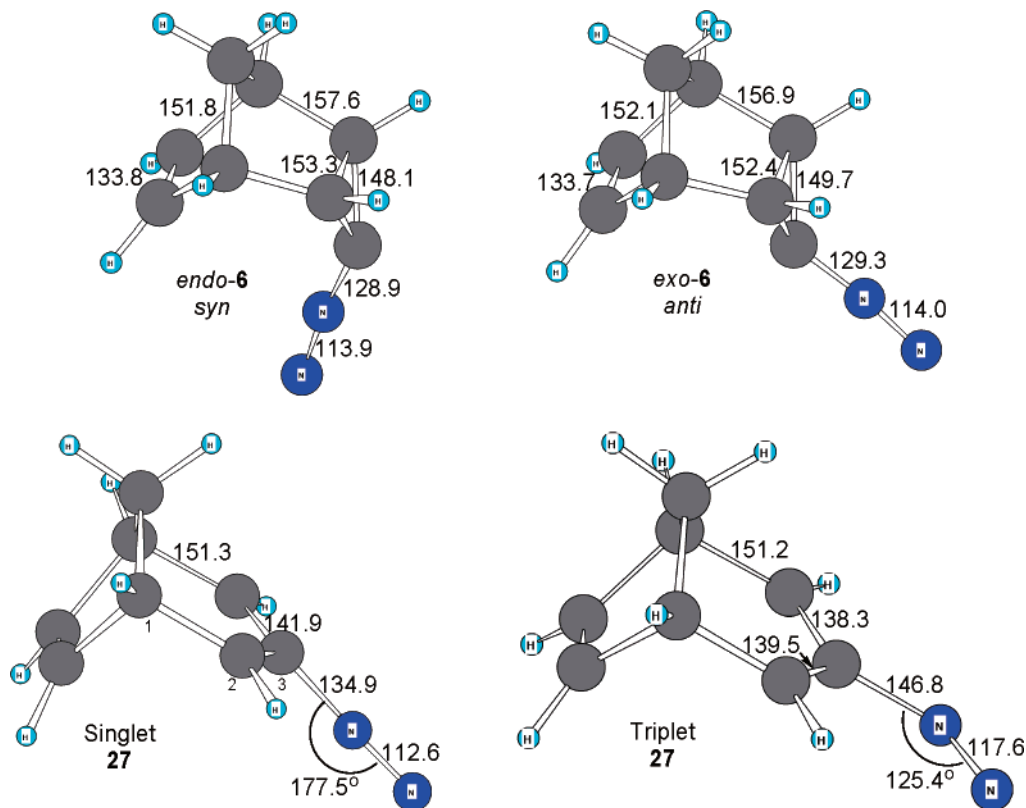


FIGURE 6. B3LYP/6-311+G(d,p) geometries of *endo*-6 and 27 with selected distances in picometers and angles in degrees.

solution, a transition state connecting *endo*-6 with allene 18, where the opening of the cyclopropane ring induces the expulsion of nitrogen. This result suggests that 27 may split nitrogen off easily.

Similarly, for *exo*-6, DFT calculations predict a loss of nitrogen to give carbene *exo*-7 by overcoming a barrier of 21.0 kcal/mol. Formation of singlet 27 requires a prohibitive 29.0 kcal/mol, and rearrangement of *exo*-6 to *endo*-6-(2-diazo vinyl)-bicyclo[3.1.0]hex-2-ene (26) requires even more energy (36.1 kcal/mol). Considering that *exo*-7 only can lead to the formation of 18 (barrier: 0.1 kcal/mol, see Supporting Information), the presence of alkyne 17 after treatment of *exo*-6 with 2 M NaOMe/MeOH can only result from rearrangement of bicyclic allene 18 (Figure 3).

Diazo compounds 6 present a remarkable geometry (Figure 6). Because of the strain of the cyclopropane ring, C3 no longer has a trigonal planar coordination such as in sp^2 hybridized systems, but it is significantly pyramidalized: the dihedral angle (C3–C2–C4–N1) ranges between 15.7° and 23.3° for the four minima shown in Figure 5. Moreover, this change in geometry is also reflected in the electron population. In the pyramidalized structure of the most stable conformer of *endo*-6, C3 is partially negatively charged (APT, -0.608 ; NBO, -0.093), a value that can be compared with the APT value of -0.244 (NBO, -0.021) found for 2-diazopropane. Our results are in good agreement with a computational investigation of diazocyclopropane performed recently by Baskir et al.,⁴³ with the exception of the absolute charge distribution. The differences in the structures are reflected not only in the enhanced reactivity of diazocyclopropanes toward 1,3 dipolar cycloadditions but also toward

extrusion of nitrogen to the corresponding carbenes.⁴⁴ However, it is worth noting that among a variety of methods and basis sets available it is possible to use a methodology providing a planar structure for diazocyclopropanes to investigate the properties of these structures. For this purpose, Ball and Kapur recommend the use of HF/D95 and HF/D95V.⁴⁵

Like 6, 27 is also a striking compound because it belongs to a new class of non-Kekulé compounds, i.e., the diazoallyls. The name for these species is coined in analogy to the well-known oxyallyls for which it has been shown that the oxyallylic form of bicyclo[2.1.0]pentan-5-one is more stable than the ketone itself.⁴⁶ Diradical 27 exists in a triplet ground state with a triplet singlet gap of 10.2 kcal/mol. The triplet possesses a long C–N bond of 146.8 pm with a C–N–N angle of 125.4° (Figure 6). In the singlet, the C–N–N fragment is nearly linear. With 134.9 pm, the length of the C–N bond corresponds well with a normal C–N single bond. In both states, C1, C2, H2, C3, N1, N2, C4, H4, and C5 are nearly in the same plane. With -4.2 kcal/mol, singlet 27 is more stable than *endo*-6. However, in contrast to the oxyallyl systems which can easily recombine to the corresponding cyclopropanones, singlet 27 does not undergo

(44) (a) Jones, W. M.; Grasley, M. H.; Brey, W. S., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 2754. (b) Tomilov, Y. V.; Okonnishnikova, G. P.; Shulishov, E. V.; Nefedov, O. M. *Russ. Chem. Bull.* **2004**, *53*, 671. (c) Guseva, E. V.; Volchkov, N. V.; Shulishov, E. V.; Tomilov, Y. V.; Nefedov, O. M. *Russ. Chem. Bull.* **2004**, *53*, 1318.

(45) Kapur, N.; Ball, D. W. *THEOCHEM* **2005**, *715*, 151.

(46) (a) Ichimura, A. S.; Lahti, P. M.; Matlin, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2868. (b) Powell, H. K.; Borden, W. T. *J. Org. Chem.* **1995**, *60*, 2654. (c) Hrovat, D. A.; Rauk, A.; Sorensen, T. S.; Powell, H. K.; Borden, W. T. *J. Am. Chem. Soc.* **1996**, *118*, 4159. (d) Hess, B. A., Jr.; Smentek, L. *Eur. J. Org. Chem.* **1999**, 3363. (e) Matlin, A. R.; Lahti, P. M.; Appella, D.; Straumanis, A.; Lin, S.; Patel, H.; Jin, K.; Schrieber, K. P.; Pauls, J.; Raulerson, P. *J. Am. Chem. Soc.* **1999**, *121*, 2164.

(43) Baskir, E. G.; Klimenko, I. P.; Tomilov, Y. V.; Nefedov, O. M. *Russ. Chem. Bull.* **2005**, *54*, 1100.

ring closure to **6**. Because of the potential decomposition in two thermodynamically stable molecules, an allene and N₂, singlet diazoallyls can only exist if the corresponding allene is strained, i.e., if it is incorporated into a small cyclic system. Therefore, one can expect that species such as 2-diazocyclopentane-1,3-diyl should be more stable toward nitrogen extrusion. Furthermore, cyclic hydrazone and oxime derivatives are also promising precursors toward this goal.

Conclusion

endo-3-Diazotricyclo[3.2.1.0^{2,4}]oct-6-ene (*endo*-**6**) already has been prepared in solution under basic conditions from the corresponding *N*-nitrosourea.⁹ According to the calculations presented here, this diazo compound presents an unusual geometry at C3 attached to nitrogen. Carbon atom C3 is strongly pyramidalized and is more negatively charged than that in a usual diazo compound. An isomeric structure resulting from ring opening of the cyclopropane moiety, i.e., the diazoallyl **27**, was also found. With -4.2 kcal/mol, **27** is more stable than *endo*-**6** and possesses a triplet ground state. However, it is separated from **6** by a high energy barrier. Diazo compound

endo-**6** easily produces carbene *endo*-**7** which rapidly undergoes a number of rearrangements. Especially, the neutral C₈H₈ species **4** comprising a pyramidally tetracoordinated carbon is expected to be generated. The highly strained species **4** rearranges to **15** which is trapped as methyl ethers **25**. In this system, a two-step mechanism via carbocations is preferred over a concerted insertion of the corresponding carbenes into the O–H bond of methanol. Moreover, this investigation suggests that the reaction rates for protonation of alkylcarbenes in alkaline MeOH are comparable to the reaction rates of the extremely fast rearranging species **4**, **7**, **14**, and **14a**.

Acknowledgment. Calculations with Gaussian 03 were performed on the Schrödinger II and III Linux clusters at the University of Vienna. The reviewers of this report were very helpful.

Supporting Information Available: Cartesian coordinates for all relevant stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO061082Y