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Synthesis and Chemistry of Bicyclo[4.1.0]hept-1,6-ene†

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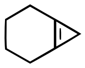
Bicyclo[4.1.0]hept-1,6-ene has been generated by elimination of 1-chloro-2-(trimethysilyl)bicyclo-[4.1.0]heptane in the gas phase over solid fluoride at 25 °C. The cyclopropene dimerizes by a rapid ene reaction forming two diastereomeric cyclopropenes. In tetrahydrofuran or chloroform the ene dimers couple to form a single crystalline triene tetramer, whereas a mixture of tricyclohexane tetramers is formed when the neat dimers are allowed to warm to room temperature. Oxidation by dimethyldioxirane or dioxygen gives carbonyl products. Quantum mechanical calculations yielded an increase in strain of ∼17 kcal/mol over that for 1,2-dimethylcyclopropene. The potential enegy barrier to flexing (folding) along the fused double bond of bicyclo[4.1.0]hept-1,6-ene is only ∼1 kcal/mol at the highest level of theory investigated.

Alkenes in which the double bonds are distorted or pyramidalized as in the 1,2-bridged cyclopropenes **1**−**4**[1,2] are of theoretical interest and usually present a considerable challenge with regard to synthesis.[3] The early theoretical work of Wagner et al.,[4] which led to the prediction that pyramidalization might be important for those compounds in which cyclopropene is fused to small rings, has been followed by more recent calculations[1,3] dealing with strain, inversion barriers, bond properties, and atom properties. Both studies found that bicycloheptene **1** and bicyclohexene **2** are fairly normal compounds except for their high strain energy. Bicyclopentene **3** may be a transition state for the carbon scrambling of methylenecyclobutylidene, and bicyclobutene **4** has an unusual structure and charge-density distribution. The structure and vibrational frequencies for **4** have also been studied by Hess et al.[5]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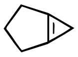
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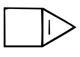
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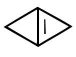
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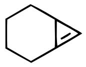
Wiberg, Artis, and Bonneville[3] have shown recently that bicyclo[4.1.0]hept-1,6-ene (**1**) can be generated in solution by dehalogenation of 1,6-dihalobicyclo[4.1.0]-heptane and trapped as the Diels−Alder adduct of 1,3-diphenylisobenzofuran. In the absence of a trapping reagent, a rapid ene reaction led to the formation of dimers which then formed tetrameric products. When the dehalogenation reaction was carried out in the gas phase using either potassium atoms or solid methyllithium, 3-methylenecyclohexene was formed. The gas phase elimination of β-halocyclopropylsilanes over solid fluoride provides an alternative route to reactive intermediates.[6] In this paper, we report the synthesis of bicyclo[4.1.0]hept-1,6-ene (**1**) under the conditions used recently to define the chemistry of bicyclo[4.1.0]hept-1,7-ene (**5**),[7] a somewhat less reactive isomer of **1**.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Results and Discussion

The synthesis of the starting material **6** is illustrated in Scheme 1. The key intermediate in this synthesis is 1-chloro-2-(trimethylsilyl)cyclopropene (**7**), which was itself prepared by the gas phase dehalogenation of **8** using solid methyllithium on glass helices.[6] Catalytic reduction of the Diels−Alder adduct of **7** and 1,3-butadiene, compound **9**, provided the desired starting compound **6**.

Elimination of **6** (Scheme 2) over solid fluoride at 25 °C and 10 mTorr yielded a 1:2 mixture of the remarkably stable ene dimers **10** and **11**.[8] The formation of two diastereomers from **1** stands in contrast to **5**, which gives only **10**.[7] As expected, it was not possible to detect **1** by low-temperature NMR spectroscopy.

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† Dedicated to Professor Richard Neidlein on the occasion of his 65th birthday.

⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1995.

(1) Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85.

(2) For other compounds in which structural constraints leads to pyramidalization see: Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 2194. Eaton, P. E.; Maggini, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 7230. Renzoni, G. E.; Yin, J.-K.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 7121.

(3) Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* **1991**, *113*, 7969.

(4) Wagner, H. U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 1210.

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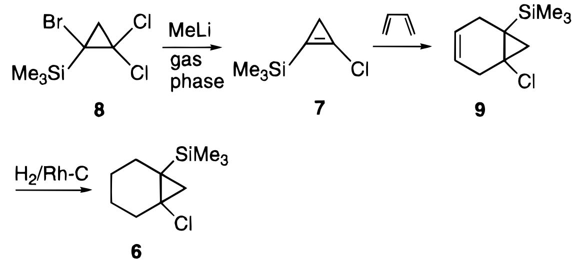
(6) Billups, W. E.; Lin, L.-J. *Tetrahedron* **1986**, *42*, 1575. See also: Lacombe, S.; Gondeau, D.; Cabioch, J.-L.; Pellerin, B.; Denis, J. M.; Pfister Guillouzo, *J. Am. Chem. Soc.* **1988**, *110*, 6964. Chan, T. H.; Massuda, D. *Tetrahedron Lett.* **1975**, 3383.

(7) Billups, W. E.; Lee, G.-A.; Arney, B. E., Jr.; Whitmire, K. J. *J. Am. Chem. Soc.* **1991**, *113*, 7980.

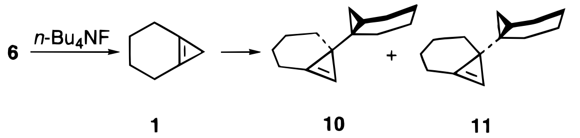
(8) For earlier examples of ene dimers from cyclopropenes see: Breslow, R.; Dowd, P. *J. Am. Chem. Soc.* **1963**, *85*, 2729. Yoshida, Z.; Miyahara, H. *Chem. Lett.* **1972**, 335. Garratt, P. J.; Tsotinis, A. *J. Org. Chem.* **1990**, *55*, 84.

0022-3263/96/1961-0764$12.00/0

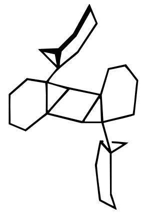
Scheme 1



Scheme 2



The ^1H NMR spectra of the ene dimers are presented in Figure 1 (spectrum A). Spectrum B was recorded using pure **10** (isolated from **5**). Stereochemical assignments were made on the basis of the tricyclohexane tetramers **12** and **13** which formed when **10** was allowed to stand at room temperature for several days. The carbon connectivities for each compound were determined earlier[7] by X-ray crystallography and found to correspond uniquely to **10**. Since cyclopropenes **10** and **11** have a diastereomeric relationship, the structure of **11** would differ in configuration at the quaternary cyclopropenyl carbon. As expected from the earlier work,[7] several tricyclohexanes were formed when the mixture of **10** and **11** from Scheme 2 was allowed to warm to room temperature. Experiments to isolate these tricyclohexanes were not carried out.



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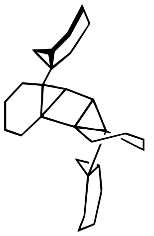

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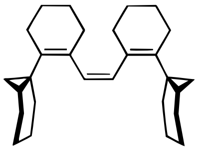
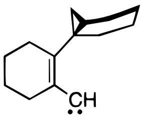
In solution (tetrahydrofuran or $CHCl_3$), the ene dimers were observed to give the same triene tetramer observed when 1,6-diiodobicyclo[4.1.0]heptane was treated with methyllithium in ether.[3] The triene can be isolated as a white crystalline solid, mp 128−129 °C. Unfortunately, we have not been able to prepare a suitable single crystal for X-ray analysis. However, the sharp melting point supports the assumption that this compound is a single isomer.[9] Compound **14** is a possible structure.



14

The formation and isomerization of a tricyclohexane tetramer as suggested earlier[3] may provide a route to **14**. Alternatively, 1,4-diyl intermediates which are presumably involved in the formation of the tricyclohexanes could undergo β-cleavage to give the triene if the cleavage was to occur fast enough to give only one configuration about the central double bond. A reaction of this type has been observed by Padwa et al.[10] Molecular models reveal that cleavage of the 1,4-diyls from various regiochemical combinations of **10** and **11** would probably yield the *meso* isomer **14**.

It is also possible that carbenes intervene as reactive intermediates in the reactions of **10** and **11**.[11] Cleavage of the cyclopropene ring may occur in either one of two ways, forming carbenes **15** or **16**. If the carbenes were to reclose, an equilibrium mixture of the cyclopropenes would probably result. We find no evidence for the interconversion of **10** and **11** as shown by the NMR spectral data presented in Figure 1. In addition, the Kirsme test[12] for carbene ylides also proved to be negative. Thus, when **10** was added to oxetane, no products from a Stevens-like rearrangement of the expected carbene ylide could be isolated.



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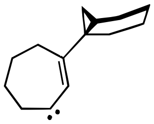

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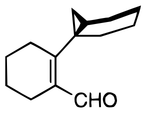
Epoxidation Using Dimethyldioxirane.[13,14] Previous studies have shown that exposure of the ene dimers to dioxygen leads to the carbonyl derivatives **17** and **18**.[3]



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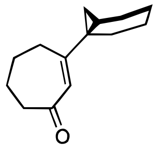

18

Although it has been suggested that carbenes **15** and **16** may be implicated as intermediates in these reactions,[15] the evidence presented above mitigates strongly against carbenes as precursors to the carbonyl compounds. A more reasonable route to the carbonyl derivatives would probably involve reactions of the cyclopropenes themselves with dioxygen.[3]

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[9] A compound with the ^1H NMR identical to **14** could be isolated from the mixture of products formed when **17** was treated with $TiCl_3$/Li. See: McMurry, J. E. *Acc. Chem. Res.* **1983**, 16, 405.

[10] Padwa, A.; Kennedy, G. D.; Newkome, G. R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1983**, *105*, 137.

[11] For recent reviews describing the interconversion of cyclopropenes with vinyl carbenes see: Halton, B.; Banwell, M. In *The Chemistry of functional Groups*: *The Chemistry of the Cyclopropyl group*; Rappoport, Z., Ed.; Wiley Interscience: Chichester, 1987; pp 1224−1321. Baird, M. S. Functionalized Cyclopropenes as Synthetic Intermediates. In *Topics in Current Chemistry*; de Meijere, A., Ed.; Springer-Verlag: Berlin, 1988; Vol. 144. Baird, M. S. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press Limited: London, 1991; pp 65−116.

[12] Kirsme, W.; Lelgemann, R.; Friedrich, K. *Chem. Ber.* **1991**, *124*, 1853.

[13] Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

[14] Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377.

[15] For reactions of carbenes with dioxygen to yield carbonyl compounds see: Bartlett, P. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1962**, *84*, 3408. Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964; p 58. Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391. Girard, M.; Griller, D. *J. Phys. Chem.* **1986**, *90*, 6801. Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 161.

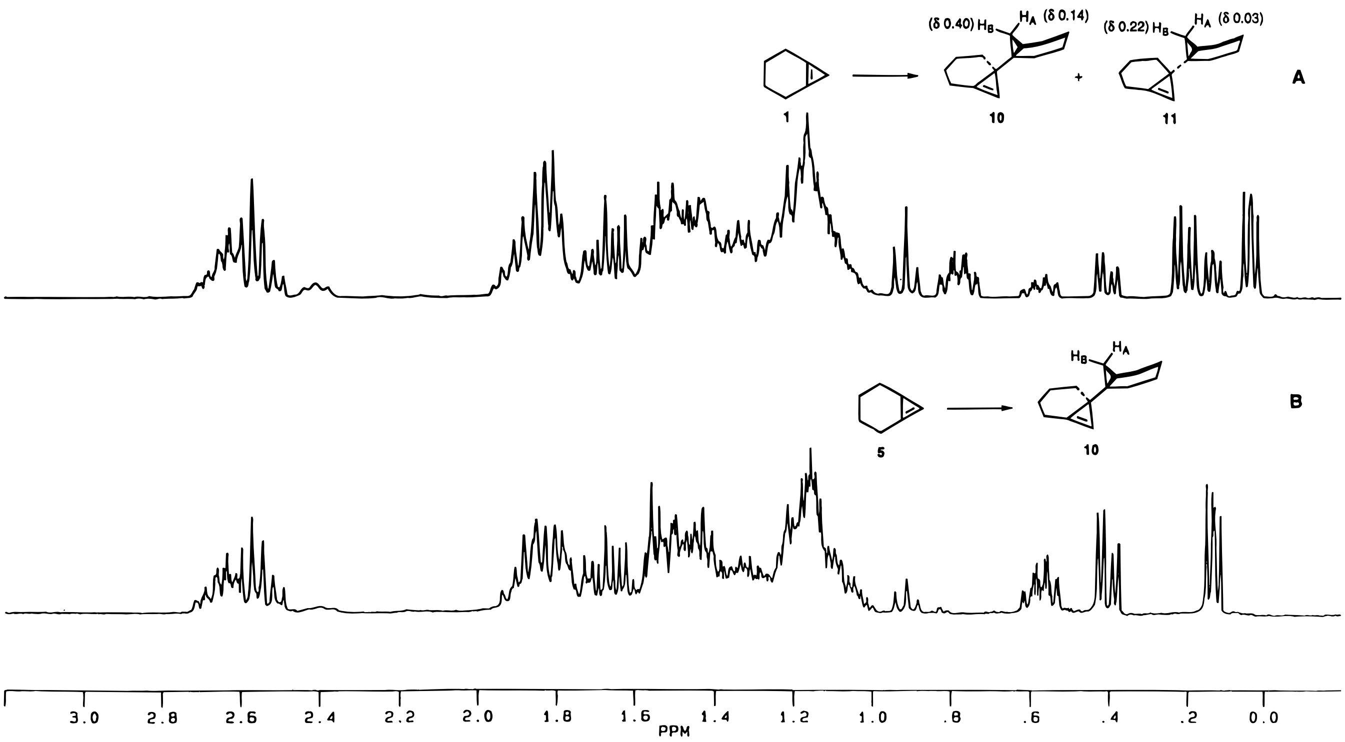
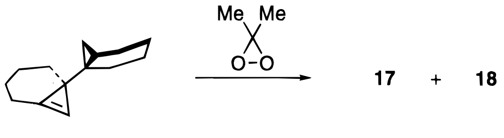


Figure 1. ^{1}H NMR spectrum (250 MHz, CDCl$_3$, 25 °C) of the ene dimers **10** and **11** obtained from **1** (spectrum A) and of **10** obtained from **5** (spectrum B). The cyclopropenyl proton of each dimer appears as a sharp singlet at δ 6.83. The signals at δ 0.9 and 2.4 can be assigned to tributylamine, a decomposition product of tetra-*n*-butylammonium fluoride.

Epoxidation of **10** using dimethyldioxirane gave **17** and **18** in about the same ratio as that observed when the cyclopropenes were exposed to dioxygen. This result may be explained by assuming the intermedicay of either the oxabicyclobutane derivative **19** or biradical intermediates of the type invoked by Frederich[16] in his extensive studies on the epoxidation of cyclopropenes by peracids to yield carbonyl compounds. A single attempt to detect **19** by low-temperature nuclear magnetic resonance spectroscopy was unsuccessful. However, when a solution of dimethyldioxirane and **10** in acetone was warmed above ~−80 °C, signals arising from both **17** and **18** could be observed, suggesting that if **19** is formed, rearrangement to the carbonyl compounds is an extremely facile process.



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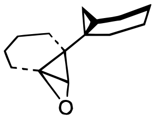

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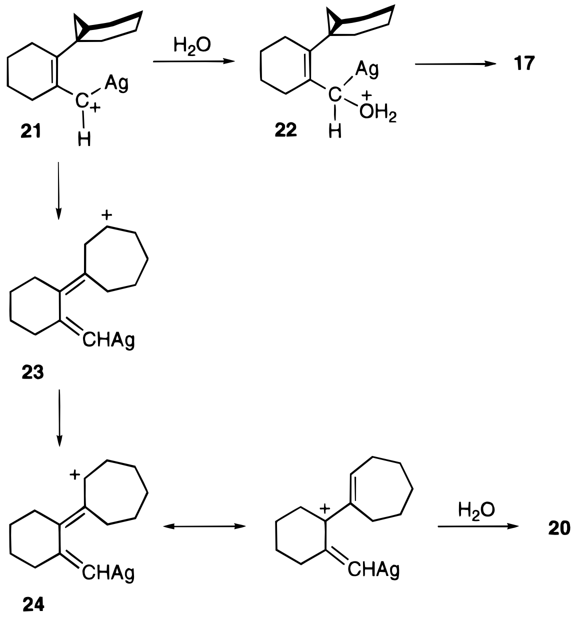
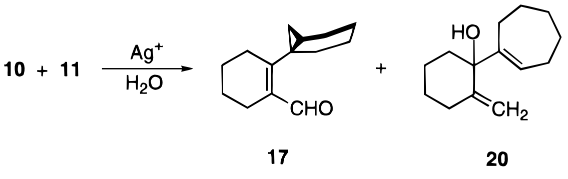
Scheme 3



Reactions with Silver Ion. The aldehyde **17** is also formed, along with **20**, when the ene dimers are reacted with aqueous silver ion. These products may be rationalized in terms of the pathways illustrated in Scheme 3. Addition of silver ion to the cyclopropenyl ring would give



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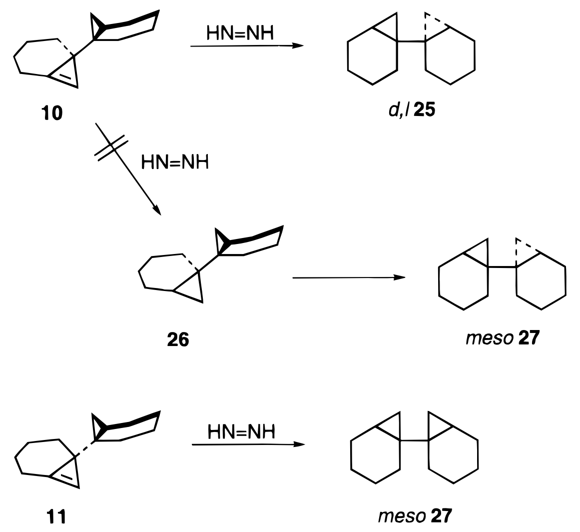
[16] Friedrich, L. E.; Leckonby, R. A.; Stout, D. M. *J. Org. Chem.* **1980**, *45*, 3198. Friedrich, L. E.; Leckonby, R. A.; Stout, D. M. *J. Org. Chem.* **1980**, *45*, 3198. Lam, Y. S. P. *J. Org. Chem.* **1978**, *43*, 604. Friedrich, L. E.; Fiato, R. A. *J. Org. Chem.* **1974**, *39*, 416. Friedrich, L. E.; Fiato, R. A. *J. Am. Chem. Soc.* **1974**, *96*, 5783.

Scheme 4



the argentocarbenium ion **21**,[17] which could react with water to give **22**. Collapse of **22** would yield the aldehyde **17**. The formation of **17** was accompanied by a precipitate of black metallic silver. The alcohol **20** is probably formed by a competing process in which **21** rearranges to **24** (via **23**) with subsequent capture of the cation by water.

Reductions Using Diimide. The cyclopropenyl double bonds of **10** and **11** can be reduced cleanly and stereospecifically by diimide.[18] Experiments with **10** proved to be the easiest since this cyclopropene can be isolated in nearly quantitative yield when **5** is generated in the gas phase, isolated at 77 K, and then allowed to warm slowly to room temperature.[2] These results are presented in Scheme 4. Isolation of the *racemic* diastereomer **25**[19] in quantitative yield can be rationalized by assuming that reduction occurs from the more hindered face of **10** (*syn* to the bicycloheptyl pendant). Reduction from the opposite face would yield the highly strained *trans*-fused[20] cyclopropane **26**. Although the intermediacy of **26** cannot be excluded, cleavage of the bridging cyclopropyl bond to a biradical with subsequent (or simultaneous) epimerization at the quaternary cyclopropyl carbon as observed for other substituted cyclopropanes[21] would yield *meso* **27**, not the *racemic* diastereomer **25** observed.

Table 1. Calculated Energies of 10, 11, and 25−27 at the RHF/6-31G*|RHF/6-31G* Level of Theory

compd	energy (in atomic units)
10	−541.674 18
11	−541.676 19
25	−542.906 06
26	−542.833 88
27	−542.911 39

The *meso* diastereomer **27** was formed, as expected, when diimide was used to reduce **11**.

Theoretical Calculations. In view of the high energy content of **10** and **11**, it is not surprising that reduction by diimide to yield the cyclopropanes occurs so readily. *Ab initio*[22−24] calculations of the ground state energies (HF/6-31G*|HF/6-31G*) of **10** and **11** show that the formation of **25** and **27** is exothermic by ~67 and ~69 kcal/mol, respectively. Epimerization of **26** at the quaternary cyclopropyl carbon to yield **27** was found to be exothermic by 45−48 kcal/mol, emphasizing the strain associated with the *trans*-fused ring system. The energies of compounds **10**, **11**, and **25−27** calculated at the RHF/6-31G* level are presented in Table 1.

The HF/6-31G*|HF/6-31G*-optimized structures of **10** and **11** are presented in Figures 2 and 3, respectively. The salient feature of these structures is the distortion from planarity by ~30° of the bonds attached to the vinyl carbons.

Optimized geometries of cyclopropene **1** were also calculated and the geometry about the bridged double bond was examined (Figure 4). A planar double bond was found at the HF/6-31G* level as determined earlier by Wiberg, Artis, and Bonneville.[3] However, inclusion of electron correlation effects in the optimized geometry (MP2(FC)/6-31G*)[23] produced small changes in the overall structure about the double bond. Pyramidalization was suggested by the folding of the two rings along the double bond (dihedral angle = 148.9°) and the lengthening of the carbon−carbon bond by about 3.3% in the optimized MP2 geometry. Density functional theory[24,25] (Becke3LYP/6-31G*) provided qualitatively similar results but with lesser folding of the rings (159.3°) and bond lengthening (2.1%).

Examination of the energies (Table 2) of optimized geometries (HF and MP2(FC)) with varying dihedral angles between the two rings revealed a nearly level potential surface from $\alpha = 130°$ to $\alpha = 230°$ (Figure 5). There were no significant barriers to folding (±50°) along the fusion of the rings, creating an extremely large window of flexibility corresponding to a normal vibrational mode of frequency of ~75 cm^{-1}. These properties can be explained readily using Wagner's analysis of the effects of bond compression on the molecular orbitals.[4]

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[17] The argentocarbenium ion **21** may be considered as a canonical form of a metal-stabilized carbene as first suggested by Gassman in connection with studies employing Rh(I). See: Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 1042. For other selected relevant references, see: Sakai, M.; Yamaguchi, H.; Masumune, S. *Chem. Commun.* **1971**, 486. Noyori, R. *Tetrahedron Lett.* **1973**, 1691. Paquette, L. A.; Wilson, S. E.; Henzel, R. P.; Allen, G. R., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 7761. Paquette, L. A.; Henzel, R. P.; Wilson, S. E. *J. Am. Chem. Soc.* **1972**, *94*, 7780. Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515, 6366.

[18] Diimide was prepared by treating dipotassium azodicarboxylate with acetic acid as described by: Kluge, A. F.; Untch, K. G.; Fried, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 9256. For other recent cyclopropene reductions using diimide see: Doyle, M. P.; Protopopova, M.; Müller, P.; Ene, D.; Shapiro, E. A. *J. Am. Chem. Soc.* **1994**, *116*, 8492.

[19] Compound **25** was identified by comparison with an authentic sample prepared by the Na/NH_3 reduction of the bis(dichlorocarbene) adduct of 1,1′-bicyclohexenyl reported by Höhn, Pickardt, and Weyerstahl. See: Höhn, J.; Pickardt, J.; Weyerstahl, P. *Chem. Ber.* **1983**, *116*, 798. The adduct prepared by these workers has been identified by X-ray crystallography as the racemic diastereomer. We thank Dr. K. E. Whitmire for determining this structure by X-ray crystallography.

[20] Chemical bonds in which cyclopropane or cyclobutane is *trans* fused to small rings of six or less vertices have been termed "twist-bent" by the late Paul Gassman. The overlap in such a bond is particularly poor, and molecules having this feature are, of course, more reactive than their *cis*-fused isomers. See: Gassman, P. G. *Chem. Commun.* **1967**, 793. Gassman, P. G.; Williams, F. J. *J. Am. Chem. Soc.* **1971**, *93*, 2704. Gassman, P. G.; Bosner, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 667. Gassman, P. G.; Bosner, S. M.; Mlinaric-Majerski, K. *J. Am. Chem. Soc.* **1989**, *111*, 2562.

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[22] SPARTAN 3.2 Programs published by Wavefunctions, Inc., 18401 Von Karman, Suite 370, Irvine, CA 92715.

[23] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

[24] Gaussian 92/DFT, Revision G.3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gompers, R.; Andres, J. I.; Raghavachari, K.; Binkley, J. S.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1993.

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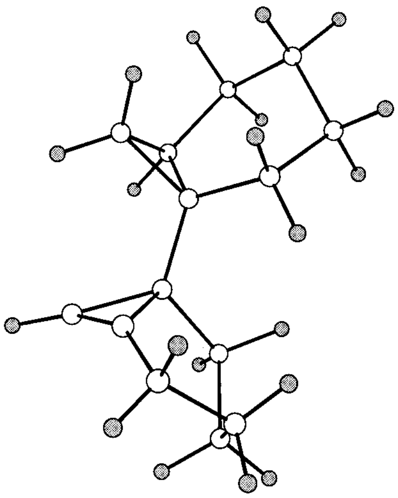
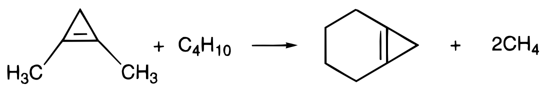


Figure 2. Calculated structure of dimer **10** at the HF6-31G*/6-31G* level.

Thus, a truly unique ground state geometry may not be definable in a physically meaningful manner.

Finally, an estimation of the strain energy of **1** is also of interest. Although several approaches to evaluate this parameter are available,[1] we have chosen the use of homoisodesmic reactions since this method is better defined than either group or atom equivalents. The heats of reaction for the two hypothetical isodesmic reactions illustrated below have been calculated. The reaction of *n*-hexane with dimethylcyclopropene may be somewhat more reliable since the bond types are better preserved. At the highest level of theory, this hypothetical reaction gives a value of nearly 18 kcal/mol. Since this represents the increase in strain over that for dimethylcyclopropene, it is perhaps not surprising that these cyclopropenes are amongst the most reactive alkenes to have been reported.



MP2(FU)/6-31G*IMP2(FC)/6-31G*

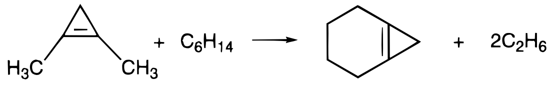
-194.58102 au -157.84497 au -271.73162 au -40.33704 au

ΔH_r = 12.73 kcal/mole

Becke3LYP/6-31G*IBecke3LYP/6-31G*

-195.26900 au -158.45803 au -272.66502 au -40.51842 au

ΔH_r = 15.79 kcal/mole



MP2(FU)/6-31G*IMP2(FC)/6-31G*

-194.58102 au -236.18611 au -271.73162 au -79.50397 au

ΔH_r = 17.30 kcal/mole

Becke3LYP/6-31G*IBecke3LYP/6-31G*

-195.26900 au -237.08546 au -272.66502 au -79.83040 au

ΔH_r = 17.97 kcal/mole

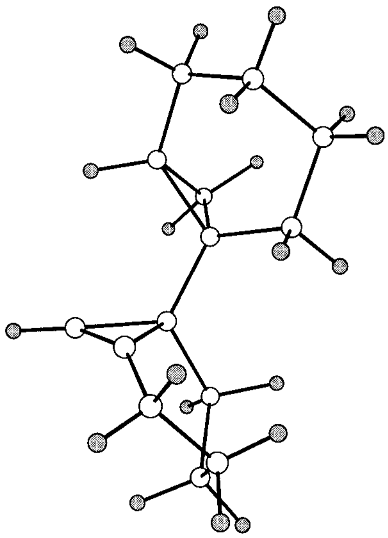
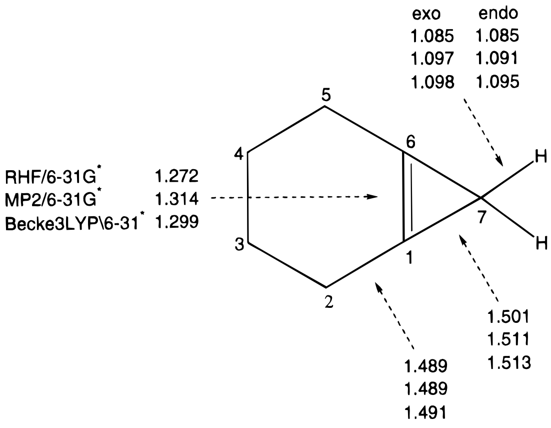


Figure 3. Calculated structure of dimer **11** at the HF6-31G*/6-31G* level.



CCC and CCH Bond Angles:	RHF/6-31G*	MP2/6-31G*	Becke3LYP/6-31G*
$C_1C_7C_6$	50.17	51.53	50.86
$C_1C_6C_7$	64.92	64.25	64.59
$C_1C_6C_5$	129.47	127.35	128.28
$C_1C_7H_1$	120.50	119.89	120.34
$C_5C_6C_7$	165.61	151.24	158.31
α	179.2	148.9	159.3

Figure 4. Calculated geometrical data (in Å and deg) for **1** from the RHF/6-31G*, MP2/6-31G*, and Becke3LYP/6-31G* methods. α denotes the dihedral angle between the two rings.

Table 2. Total Energies (in Atomic Units) of Planar and Folded 1 at Various Levels of Theory

	level of theory		
	HF/6-31G*	MP2(FC)/6-31G*	Becke3LYP/6-31G*
planar	−270.791 59[a]	−271.696 22[b]	−272.662 95[b]
folded	−270.790 54[c]	−271.697 36[a]	−272.665 02[a]
difference	0.001 05	−0.001 14	−0.002 07

[a] Fully optimized. [b] Optimized with α constrained to 180°. [c] Optimized with α constrained to 148.9°.

Experimental Section

General. Analyses were carried out as described previously.[7] Chemicals were of reagent quality and used as obtained from the manufacturers. All reactions were carried out in an atmosphere of dry nitrogen. Solvents were dried and purified as described previously.[7]

Calculations were performed using SPARTAN 3.2[23] programs and the Gaussian 92/DFT[24] programs. For **10** and **11**, the geometries were optimized with the 3-21G(*) basis set. Conformational analysis at the PM3 level was utilized to enhance the optimization, and single point energies were

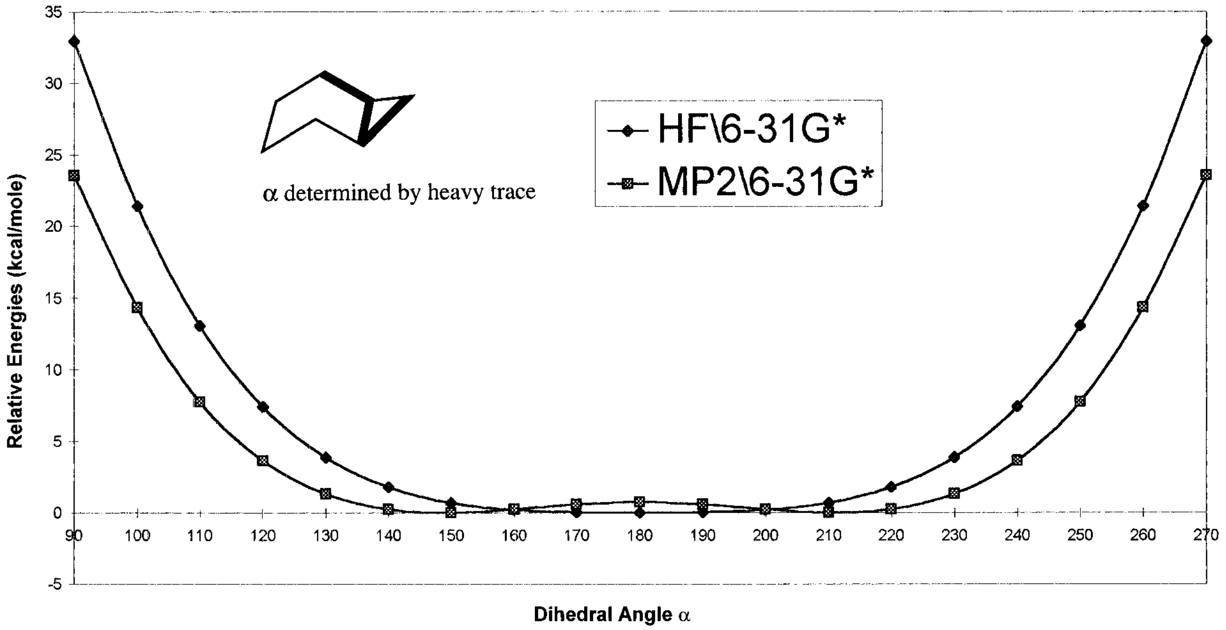


Figure 5. Optimized electronic energies calculated at various levels of theory for **1**.

calculated with the 6-31G* entended basis set. Optimized geometries on **1** were calculated with the 6-31G* extended basis set. Computation of the harmonic frequencies for fully optimized structures showed only positive frequencies, indicating they are true minima.

Preparation of 1-Chloro-6-(trimethylsilyl)bicyclo[4.1.0]heptane (6). 1-Chloro-2-(trimethylsilyl)cyclopropene (**7**) was prepared by dehalogenation of **8** (1.40 g, 5.56 mmol) over solid methyllithium at 25 °C and 10 mTorr. 1,3-Butadiene (6 mL) was then introduced into the cold trap containing the cyclopropene, and a double-ended needle was used to transfer the resulting mixture to a pressure bottle. The reaction mixture was then allowed to stand for 72 h at −20 °C, 48 h at 4 °C, and 1 day at room temperature. The excess 1,3-butadiene was removed and the product reduced over 5% Rh/C in a mixture of pentane (10 mL) and methanol (5 mL) at 50 psi for 2 h. Compound **6** was isolated by column chromatograpgy (silica gel, *n*-hexane) in 60% yield. ^{1}H NMR: δ 0.18 (s, 9H), 0.82 (d, 1H, $J = 5.7$ Hz), 1.12 (d, 1H, $J = 5.7$ Hz), 1.08−1.64 (m, 6H), 1.92−2.40 (m, 2H). ^{13}C NMR: δ −1.59, 21.98, 22.09, 23.11, 28.01, and 35.75.

Elimination of 6 over Solid Tetra-*n*-butylammonium Fluoride. Compound **6** (50 mg, 0.25 mmol) was eliminated at 25 °C to yield a 1:2 mixture of the ene dimers **10** and **11** using the general procedure described earlier. The cold trap was then warmed slowly to 0 °C. Trimethylsilyl fluoride and a small amount of 1-butene were removed *in vacuo*. The dimers were dissolved in $CDCl_3$ (0.5 mL) for spectral characterization. ^{1}H NMR of **10**: δ 6.83 (s, 1H), 2.70−2.30 (m, 2H), 2.1−0.9 (m, 14H), 0.7−0.5 (m, 1H), 0.40 (dd, 1H, $J = 9.2$, 3.7 Hz), and 0.14 (dd, 1H, $J = 3.7$, 5.4 Hz); **11:** 6.83 (s, 1H), 2.70−2.30 (m, 2H), 2.1−0.9 (m, 14H), 0.9−0.7 (m, 1H), 0.22 (dd, 1H, $J = 4.1$, 9.1 Hz), 0.03 (dd, 1H, $J = 4.1$, 7.0 Hz). ^{13}C NMR of **10:** δ 111.51, 31.15, 28.32, 24.41, 24.38, 24.20, 23.20, 21.98, 21.93, 17.56, 16.88; **11:** 111.16, 31.52, 28.37, 24.56, 24.34, 23.24, 22.07, 22.04, 18.33, and 16.41.

Synthesis of Triene 14. Compound **6**[7] (201.0 mg, 0.99 mmol) was eliminated over solid fluoride at 25 °C as described above. Tetrahydrofuran (5 mL) or chloroform (5 mL) was then distilled into the cold trap with the exclusion of dioxygen. After 7 days, the mixture was transferred to a small flask and the solvent removed *in vacuo*. The residue was purified by column chromatography (*n*-hexane) to give 78.7 mg of **14** (yield 84%) as colorless crystals, mp 128−129 °C.

Diimide Reduction of 10 and 11. The ene dimer **10** was synthesized from 7-chloro-1-(trimethylsilyl)bicyclo[4.1.0]heptane (150 mg, 0.74 mmol) as described earlier.[7] **10** was transferred under nitrogen to a flask containing dipotassium azodicarboxylate (400 mg, 2 mmol) dissolved in 3 mL of methanol. Glacial acetic acid (250 mg, 4 mmol) was then added slowly and the mixture stirred for 2 h at 0 °C and then for 30 min at room temperature. The solvent was removed *in vacuo* and the residue taken up in 8 mL of water and extracted with *n*-hexane. Workup gave *d*,*l*-1-(bicyclo[4.1.0]hept-1-yl)bicyclo[4.1.0]heptane (**25**) quantitatively. A mixture diasteromers *meso* and *dl* were obtained in the ratio of 2:1 under the similar conditions if the precusor **6** was used. **25**. ^{1}H NMR: δ 1.84−1.42 (m, 4H), 1.29−1.12 (m, 4H), 0.71−0.64 (m, 1H), 0.24 (dd, 1H, $J = 4.3$, 9.5 Hz), 0.01 (dd, 1H, $J = 4.3$, 5.5 Hz). ^{13}C NMR: δ 28.73, 25.58, 24.29, 22.50, 21.63, 15.44, 15.05. **27**. Protons of cyclopropane 0.60−0.56 (m, 1H), 0.31 (dd, $J = 4.3$, 9.5 Hz), 0.01 (m, 1H). ^{13}C NMR δ 28.88, 25.66, 24.29, 22.42, 21.63, 15.92, 14.85. MS: calcd for $C_{14}H_{22}$ *m*/*e* 190.1721, found *m*/*e* 190.1725; calcd for $^{13}CC_{13}H_{22}$ *m*/*e* 191.1726, found *m*/*e* 190.1761.

Reaction of Dimers 10 and 11 with Aqueous Silver Tetrafluoroborate. Compound **6** (300 mg, 1.4 mmol) was passed through a fluoride column at 25 °C as described before. Eight mL of freshly distilled ether was then introduced into the trap. The solution was transferred to a three-necked flask by use of a double-ended needle under nitrogen at room temperature. Silver tetrafluoroborate (525 mg, 2.7 mmol) in water (10 mL) was added, and the mixture was stirred for 3 h at room temperature. The precipitation of silver was observed immediately. The reaction mixture, consisting of aldehyde **17** and alcohol **20** (1:1), was separated by column chromatography on silica gel (*n*-hexane−dichloromethane). The products were isolated in the yield of 42%. **20**. ^{1}H NMR: δ 5.51 (bs, 1H), 4.90 (bs, 1H), 4.74 (bs, 1H), 2.55−2.21 (m, 2H), 2.20 (s, 1H), 2.1−1.9 (m, 6H), 1.85−1.70 (m, 4H), 1.55−1.27 (m, 6H). ^{13}C NMR: δ 153.69, 135.60, 126.52, 106.45, 73.89, 46.12, 40.92, 34.05, 30.12, 28.04, 25.42, 23.65, 22.86, 22.10. IR: ν 3550, 2932, 2856, 1680, 1448 cm^{-1}. MS: calcd for $C_{14}H_{22}O$ *m*/*e* 206.1665, found *m*/*e* 206.1660; calcd for $^{13}CC_{13}H_{22}O$ *m*/*e* 207.1665 found *m*/*e* 207.1697.

Epoxidation of Dimers 10 and 11 by Dimethyldioxirane. The ene dimers **10** and **11** were prepared from compound **6** (51 mg, 0.25 mmol) as described above. Degassed dimethyl dioxirane (5 mL, 0.08 M in acetone) was then introduced at −20 °C. The resulting mixture was warmed slowly to room temperature and the solvent removed *in vacuo*. Column chromatography on silica gel (methanol/acetone) yielded aldehyde **17** (3 mg, 6%) and ketone **18** (21 mg, 42%).

Coupling of Aldehyde 17 by $TiCl_3$/Li. Lithium wire (10 mg, 1.4 mmol) and $TiCl_3$ (65 mg, 0.4 mmol) were slurried in 2 mL of dry dimethoxyethane (DME) under an atmosphere of argon. The mixture was refluxed for 1 h and then cooled to room temperature. A solution of **17** (20.4 mg, 0.1 mmol) in DME (1 mL) was added and the mixture refluxed for 2 h and cooled to room temperature. The resulting mixture was diluted with petrolum ether and filtered. The filterate was quenched with a small amount of methanol. After the solvents were removed *in vacuo*, chromatogaphy on silica gel (*n*-hexane) gave triene **14** in 48% yield.

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Supporting Information Available: Cartesian coordinates for compounds **10**, **11**, and **25**−**27**. ^{1}H and ^{13}C NMR spectra and the IR spectrum of **20** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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