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Synthesis of Precursors of a Highly Pyramidalized Alkene and *Ab Initio* Calculations on Methylenecyclopropane, Cyclopropene, and 1,3-Diradicals.

William T. G. Johnson

A dissertation submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

University of Washington

1999

Program Authorized to Offer Degree: Department of Chemistry

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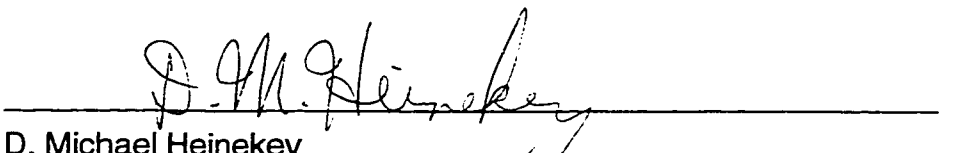

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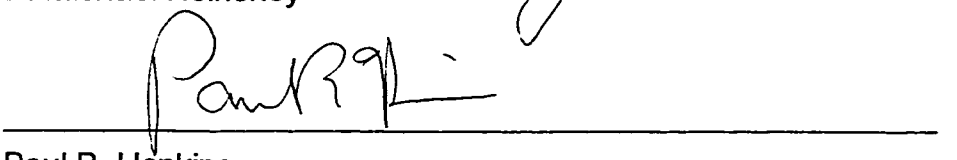

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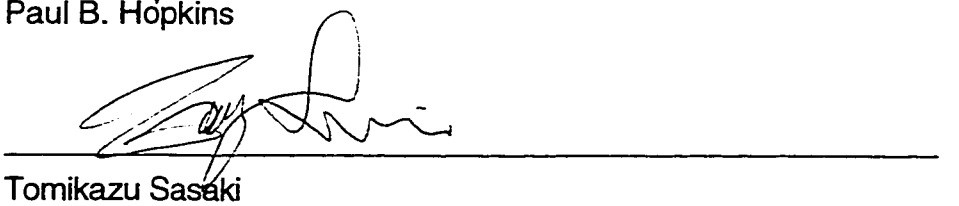

Tomikazu Sasaki

Date: July 23, 1999

University of Washington
Abstract

Synthesis of Precursors of a Highly Pyramidalized Alkene and *Ab Initio* Calculations on Methylenecyclopropane, Cyclopropene, and 1,3-Diradicals.

William T. G. Johnson

Chairperson of the Supervisory Committee:
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The synthesis of precursors for the highly pyramidalized olefin 3,7-dimethyltricyclo[3.3.0.$0^{3,7}$]octane are described within. Three computational projects are also contained in this thesis. In the first, the increase in strain energy that results from placing a trigonal center in a cyclopropane ring is shown to be due to the loss of a stabilizing cyclopropyl C-H bond, not an increase in angle strain. In the second, the singlet state of a derivative of the trimethylene diradical is shown to be stabilized to such an extent relative to the closed cyclopropane as to make the two isomers nearly isoenergetic. The barrier for closure of the trimethylene derivative via enforced disrotation is also shown to be quite high, owing to the substitution at C-2 of the diradical with silyl groups. In the third, previous experimental results are reinterpreted showing that spiropentane opens via conrotation, in agreement with qualitative molecular orbital theory. A long range interaction between a terminal methyl group in pentane-2,4-diyl and the more distant radical center is described. The interaction is found to be stabilizing when C-3 is substituted with donors, and destabilizing when C-3 is substituted with acceptors.

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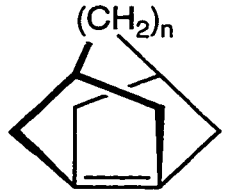
Acknowledgments

Wes Borden must be acknowledged for his efforts in training me to be a chemist. His patience and desire to teach his students is the primary reason that I have been able to attain this degree. I must also thank Dave Hrovat for his making the computational portions of my research so much simpler and easier. My parents must also be acknowledged. Their love and encouragement helped me continue in my studies despite some adversity. And I must thank my wife, without whom this work would have little meaning.

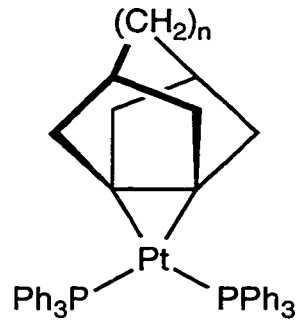
Chapter 1:

Synthesis of Precursors for 3,7-Dimethyltricyclo[3.3.0.0^{3,7}]oct-1(5)-ene (1, n = 0) and Attempted Preparation of the $(Ph_3P)_2Pt$ complex (2, n = 0)

The ideal geometry for a double bond has the olefinic carbons and the four substituents of the double bond in the same plane. Pyramidalization distorts the double bond such that the two planes formed by each of the olefinic carbons and the substituents attached to them are not coplanar, while maintaining the symmetry plane containing the axis of the double bond and bisecting the geminal pairs of substituents. Pyramidalization can occur in a *syn* fashion or in an *anti* fashion. *Syn* pyramidalized double bonds are found in some polycyclic cage compounds such as the fullerenes, and are much more common than *anti* pyramidalized double bonds; and in the following chapter, all references to pyramidalized double bonds indicate *syn* pyramidalization.



1



2

Pyramidalization changes the familiar chemistry of the double bond dramatically.[1] Dimerization of highly pyramidalized alkenes occurs rapidly,[2] and pyramidalized alkenes that do not dimerize at room temperature react with

atmospheric oxygen.[3] The normally electron-donating π bond becomes a good electron acceptor.[1,3]

Computational[4] and experimental[1] studies of an homologous series of pyramidalized olefins (**1**) have yielded information about the double bonds in these compounds. By varying the number of bridging methylene groups in **1**, different amounts of pyramidalization can be introduced into the double bond.

Pyramidalization allows the 2s AOs of the olefinic carbons to be mixed into the "π" bond. The increase in 2s character stabilizes both the π and π* MOs. However, this rehybridization also decreases the overlap of the two hybrids, as compared to the overlap of two parallel p AOs, by pointing the large lobes of the hybrids away from each other. The loss of the bonding overlap in the π MO destabilizes it. The effects of increased 2s character and reduced overlap tend to cancel, so that the energy of the π MO remains relatively constant. In contrast, reduction of antibonding overlap in π* stabilizes this MO further. Hence, the π* MO drops rapidly in energy upon pyramidalization. The unusually low energy of π* is responsible for the ease of reduction of pyramidalized alkenes, such as C_{60},[5] and for the ability of pyramidalized alkenes to form unusually stable complexes with transition metals, such as Pt(0), that can donate electron density into (backbond with) this MO.[6]

Alkenes **1**, with n = 1, 2, and 3, have been synthesized and studied by a variety of methods.[1-4] The least pyramidalized member of this series, **1**, n = 3, has provided the most information, because it does not dimerize at room temperature.[3] The ionization energy (IE) of **1**, n = 3, was found to differ from the ionizaton energy of a reference compound, bicyclo[3.3.0]oct-1(5)-ene (BCO), by only 0.31 eV, but the electron affinity (EA) of **1**, n = 3, was found to be more positive then the EA of BCO by 0.74 eV.[3]

As already noted, the electron accepting ability of **1**, n = 1 - 3, makes these alkenes good ligands for platinum(0).[1,6] The complexes, **2**, n = 1 - 3, are stable enough to study at room temperature by ^{1}H, ^{31}P, ^{13}C, and ^{195}Pt NMR spectroscopy. The spectra indicate that the ability of the alkenes, **1**, n = 1 - 3, to accept electron density from Pt(0) via back donation increased with increasing pyramidalization. The NMR spectra of the $(Ph_3P)_2Pt$ complex **2**, n = 0, should be particularly interesting, since **1**, n = 0, is the most highly pyramidalized member of this series. Based on the spectra of **2**, n = 1 - 3, one can predict that the chemical shift of the phosphines in **1**, n = 0, should be about δ 30. The one bond coupling constant, $^{1}J_{P\text{-}Pt}$ should be the smallest observed in the series, with a magnitude less than 2960 Hz, found in **2**, n = 1. The next section of this thesis describes an attempted preparation of this complex.

Alkenes **1**, n = 1 - 3, all have a weak absorption in the IR corresponding to the double bond stretch. The pyramidalization of the double bond creates a dipole moment along the *z*-axis in the standard orientation of the molecule, and upon transition to a higher vibrational level, a modest change in this dipole moment occurs. For **1**, n = 1- 3, this stretch has been observed at, respectively, 1496,[7] 1560[8] and 1615[3] cm^{-1}. These absorptions are substantially lower in frequency than the double bond stretch seen at 1680 cm^{-1} in the Raman spectrum of BCO.

The UV spectra of these compounds are also unusual. The lowering of π^* relative to π causes these alkenes to absorb at longer wavelengths than BCO. This effect has been verified for **1**, n = 2,[8] and 3,[3] which have maxima in their UV spectra at 245 nm and 217 nm, respectively. As a comparison, BCO does not have a UV maximum above 200 nm. Using electron-energy-loss (EELS) spectroscopy,[9] the difference in energy between the ground and first excited singlet and triplet states can be measured. For the excited singlet state of **3**, n = 3, this energy difference was

found to be 5.4 eV (230 nm).[10] The presence of pentane as a solvent causes a blue shift in the previously observed solution UV spectrum that is absent in the gas-phase EELS spectrum.

A bis-ethano derivative (**3**) of **1**, n = 0, has been previously prepared.[2b] Dehalogenation of a vicinal diiodide precursor with alkyl lithium in the presence of diphenylisobenzofuran (DPIBF) gave the anticipated Diels-Alder adduct in quantitative yield. However, no spectral data on **3** was obtained.

3

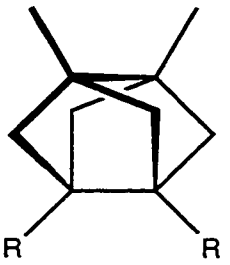
Since **1**, n = 0, is the most highly pyramidalized member of the series, matrix isolation of this alkene, in order to measure its IR and UV spectra, is highly desirable. The preparation of a precursor of a dimethyl derivative of **1**, n = 0, that could be used for this purpose is described in this thesis.

Synthesis of 1,5-Diiodo-3,7-dimethyltricyclo[3.3.0.0^{3,7}]octane (3, n = 0)

The synthesis of **2**, n = 1, 2, and 3, have been achieved by reducing a vicinal diiodide or vicinal dimesylate with sodium amalgam in the presence of bis(triphenylphosphine)(ethylene)platinum(0).[6]

The first attempt to synthesize a derivative of **2**, n = 0, used the same approach. Diol **6** is readily synthetically accessible by a samarium(II) iodide[11] reduction of 1,5-dimethylbicyclo[3.3.0]-octane-3,7-dione (**9**, see Figure 1.1), which is easily prepared in two steps from commercially available compounds. Conversion of diol **6** to dimesylate **5** and exposure of the latter to sodium amalgam returned

starting material. The bistriflate was also prepared, but it too survived reduction with sodium amalgam unchanged.



4 R = I
5 R = OH
6 R = OMs
7 R = CO_2CH_3
8 R-R = C(O)OC(O)

The disappointing results with the derivatives of diol **5** led us to attempt the synthesis of diiodide **4**. Starting from **9** and following literature procedures[12] with only minor modifications leads to diester **7**, which we were able to convert to **4** in two additional steps. The synthesis of **4** is outlined in Figure 1.1.

Dione **9** was converted to a biscyanohydrin by treatment with aqueous sodium cyanide and subsequent acidification. Elimination of water gave bis-α,β-unsaturated nitrile, **10**, which was reduced with hydrogen gas over palladium to the aliphatic nitrile and hydrolyzed. Treatment of the diacid with diazomethane yielded diester, **11**. Deprotonation of **11** with two equivalents of LDA removed both α hydrogens, and oxidation of the dianion with iodine gave **7**, albeit in poor yield. Hydrolysis of the ester groups in **7** followed by a double Hunsdieker reaction of the resulting diacid, **12**, yielded **4**. The same method for converting **7** to **4** was subsequently published by Camps, *et. al.*, who generated the dimethyl derivative of **1**, n = 0, by allowing **4** to react with *t*-butyl lithium.[13]

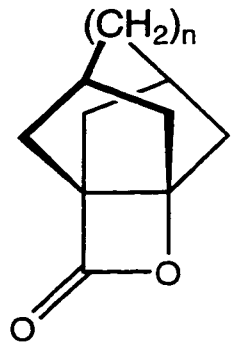
Reduction of **4** with sodium amalgam in the presence of bis(triphenylphosphine)(ethylene)platinum(0) produced a mixture of products with a complex ^{1}H NMR spectrum. However, in the ^{31}P NMR spectrum an apparent triplet, at δ 30.5, with $^{1}J_{P\text{-}Pt}$ = 2850 Hz was observed. For **2**, n = 1, 2, and 3, the direct P-Pt coupling constants are 2960 Hz, 3115 Hz, and 3332 Hz, respectively; and the chemical shifts for the phosphines are δ 30.5, 31.1, and 32.2. Therefore, both the ^{31}P chemical shift of the triplet and the Pt-P coupling constant suggest that the desired complex is formed. In the ^{1}H NMR two AB resonances are visible at δ = 2.1 and 1.7 with $^{2}J_{H\text{-}H}$ of 8 Hz. The former resonance also appears to possess platinum satellites with a $^{2}J_{H\text{-}Pt}$ of 21.0 Hz. These ^{1}H NMR signals could be due to the geminal pairs of hydrogens in the coordinated alkene in the complex.

The ^{31}P resonance slowly disappeared over a period of three weeks if the crude complex was left in a sealed NMR tube in $CDCl_3$. Repeated attempts at recrystalization of the crude complex never yielded a pure enough sample to give an interpretable ^{13}C NMR spectrum. Given the difficulty in purifying this compound, and its apparent instability, the attempted preparation of this dimethyl derivative of **2**, n = 0, was abandoned.

Synthesis of 3,7-Dimethyltricyclo[3.3.0.0^{3,7}]octane-1,5-dicarboxylic anhydride (8)

Although we were unable to use diiodide **4** to prepare the dimethyl derivative of **2**, n = 0, we hoped that **4** or one of the other compounds in Figure 1.1 might be useful for generating the uncomplexed alkene under conditions where it could be matrix isolated and its IR and UV spectra obtained. Pyrolysis of β-lactone, **13**, n = 2, allowed matrix isolation of **1**, n = 2, which enabled the IR and UV spectra of the alkene to be measured.[8] However, pyrolysis of **13**, n = 1, did not give **1**, n =

1, as hoped for but instead yielded a keto ketene by an alternative cleavage of the β-lactone ring.[2a] Presumably, this preference is due to the high energy of the pyramidalized double bond in **1**, n = 1. Upon increasing the temperature above 550°C, CO_2 was lost, but **1**, n = 1, underwent a rearrangement to yield the observed product, 2,6-dimethylenebicyclo[2.2.1]heptane. A similar rearrangement was observed during the pyrolysis of **13**, n = 2, at elevated temperatures. Therefore, β-lactone pyrolysis is unlikely to be a satisfactory method for generating **1**, n = 0.



13

By using an anhydride as a precursor for **1**, n = 0, the above difficulty may be avoided. The likeliest bond cleavage forseen for anhydride **8** upon either pyrolysis or photolysis is C-O σ bond breaking to form carboxyl and carbonyl radicals. The lifetimes of carboxyl radicals are known to be rather short[14] and so it is hoped that the loss of CO_2 from this diradical will be rapid. Should the C1 - C5 σ bond also cleave, a ketene would be formed from **8**, but where this cleavage also forms a carbonyl in the case of **13**, a carbene would be formed from **8**. We therefore believe that this alternative reaction path will be slower in **8** than in **13**. Subsequent loss of CO from the pyramidalized olefin may then occur at low enough temperature to allow the isolation of **1**, n = 0.

Treatment of 3,7-dimethyltricyclo[3.3.0.0^{3,7}]octane-1,5-dicarboxylic acid with thionyl chloride using a modification of the method of Carpenter for the synthesis of cinnamic anhydride,[15] gave **8** in 51% yield. Anhydride **8** was characterized by ^{1}H NMR, ^{13}C NMR, IR, and high resolution FAB MS. Several samples have been sent to Professor Wolfram Sander at the University of Bochum where he will flash vacuum pyrolyze **8** in the hope that it will lose CO and CO_2 and allow the matrix isolation of the dimethyl derivative of **1**, n = 0. He will also investigate the photolysis of **8**, n = 0, in matrix isolation in the hope of forming this alkene and obtaining its IR and UV spectra.

Experimental

Much of the synthetic work presented below has been published previously by others.[16,13,14] The presentation here summarizes my modifications and offers caveats to future laborers. All the reagents for the synthesis of diiodide **4** and anhydride **8** were obtained from Aldrich and used without purification. THF and diisopropyl amine were dried over sodium. For other reactions the solvents were used as obtained unless otherwise specified. NMR spectra were recorded on Bruker 200 MHz, 300 MHz, or 500 MHz spectrometers.

cis 1,5-Dimethylbicyclo[3.3.0]octane-3,7-dione (9)

In a 500 ml Erlenmeyer flask equipped with a magnetic stir bar, 2.94 g (35 mmol) of sodium bicarbonate was dissolved in 200 mL of deionized water. Dimethyl acetone-1,3-dicarboxylate (30 mL, 204 mmol) and 8.5 mL (97 mmol) of biacetyl were then added to the stirring solution. After addition of the biacetyl, the characteristic yellow color of the starting material fades and is replaced with an opaque orange. The Erlenmeyer was covered to keep out dust and left to stir

overnight. Vacuum filtration the following day yielded 33.0 g (83 mmol) of tetramethyl 3,7-dihydroxy-1,5-dimethylbicyclo[3.3.0]octa-2,6-diene-2,4,6,8-tetracarboxylate and its C_s isomer. (86 % yield) m.p. = 155 - 158°C (decomp.) ^{1}H NMR ($CDCl_3$, 200 MHz)δ 1.30 (s, 6H), δ 3.75 (s, 6H), δ 3.88 (s, 6H), δ 3.95 (s, 2H), δ 10.5 (s, 2H). The mixture of tetraesters was then decarboxylated by suspending it in 264 mL of 1M HCl (aq) and 52 mL glacial acetic acid and heating at reflux for several hours in a 2L flask. An overly large flask is necessary to prevent the reaction from erupting into the condensor upon decarboxylation. The reaction time may vary. The reaction is finished when a clear solution is obtained with no solids. The vessel was then cooled and the volume of the reaction was reduced by evaporation of acetic acid and water under reduced pressure. The remaining aqueous layer was extracted with methylene chloride, and the combined organics were washed with sat. aq. $NaHCO_3$ until the aqueous layer remained at neutral pH. The organic layer was then washed with sat. aq. NaCl and dried over anhydrous $MgSO_4$. Solvents were removed under reduced pressure to afford 11.0 g of **9**. (80% yield, 69% yield overall, lit. yield 74%[16]). m.p. 218-221°C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.17 (s, 6H), δ 2.32 (AB, 8H).

cis 1,5-Dimethylbicyclo[3.3.0]octa-2,6-diene-3,7-dicarbonitrile and its C_s isomer (10)

In a 250 mL boiling flask equipped with a magnetic stir bar (with no cuts in its teflon cover) and a 125 mL addition funnel, was placed 22.9 g (467 mmol) of NaCN, 11.0 g (66 mmol) of **10**, and 60 mL of deionized water. The vessel was then cooled with an ice bath and the temperature was maintained between 5 and 15°C for the duration of the reaction. Over four hours a mixture of 40 mL conc. H_2SO_4 and 60 mL water was added to the slurry with constant stirring. Using a single

neck reaction vessel and a non-pressure equalizing addition funnel fitted with a glass stopper ensured a slow addition, as well as a closed atmosphere for containing HCN vapors. After twenty minutes the slurry turned a golden yellow. After 1.5 hours a white solid had formed floating in a dark brown liquid. The reaction mixture was poured into a 500 mL separatory funnel with an additional 80 mL of water. The aqueous layer was extracted with three 100 mL portions of ethyl acetate. The combined organics were washed with water, and sat. aq. NaCl, and then dried over $MgSO_4$. Volatile organics were evaporated under an airstream in the hood overnight by placing the product solution in a 500 mL Erlenmeyer and placing the flask in a gently heated water bath. All aqueous waste and glassware should be immediately treated with bleach to oxidize any cyanide still present to cyanate.

The dark-brown viscous residue remaining after overnight evaporation was dissolved in 220 mL pyridine and placed in a 500 mL 3-neck round bottom flask equipped with a magnetic stir bar, a condenser, and a 125 mL addition funnel. The flask was then heated in an oil bath to reflux at 140°C. $POCl_3$ (42 mL, 450 mmol) was then added dropwise to the refluxing reaction mixture. Initially much heat is liberated by this addition as the $POCl_3$ consumes residual water in the reaction mixture. The reaction becomes very dark as the $POCl_3$ is added. After the addition is complete the reaction is allowed to reflux for 8 hours. At which point, the reaction is cooled to < 5°C in an ice bath and then poured onto a mixture of 162 g ice and 126 mL conc. HCl, also cooled in an ice bath. This quenching must be done with caution as much heat is liberated as the $POCl_3$ is consumed. The quenched reaction mixture is then cooled to < 5°C in an ice bath and vacuum filtered. The solubility of the product is surprisingly dependent on the precise amounts of water, HCl, and pyridine present. The brown solid is collected and dissolved in CH_2Cl_2. The slurry is then vacuum filtered using Celite as an aid to remove much of a potent emulsification

agent suspended in the organics. The filtrate is then washed with water, sat. aq. NaCl, and dried over $MgSO_4$. The CH_2Cl_2 was removed under reduced pressure affording 7.67 g of the crude, but synthetically useful product. Recrystalization from ether yielded 7.13 g (39 mmol) of pure material in two crops. (59% yield, lit. yield 63%[12]) m.p. 111-114°C (despite the presence of two isomers the melting range was only three degrees) ^1H NMR ($CDCl_3$, 200 MHz) δ 1.18 - 1.11 (m, 6H), δ 2.70 - 2.46 (m, 4H), δ 6.31 (s, 2H).

cis 1,5-Dimethylbicyclo[3.3.0]octane-3,7-dicarbonitrile as a mixture of diastereomers

To a 500 mL Parr hydrogenation flask, 0.6 g of 10% Pd on charcoal was added. A mixture of the two isomers of **10** (7.67 g, 42 mmol) was dissolved in 100 mL ethanol was then added to the flask. The catalyst should be added to the flask before the solvent to prevent fire. The vessel was pressurized to 50 psi of H_2 (as judged by the regulator on the hydrogen tank) and shaken for several days on a Parr hydrogenator. Progress was monitored by the disappearance of the vinylic resonance in the ^1H NMR. The reaction afforded 7.68 g (41 mmol) of the nitrile. (98% yield, lit. yield 100%[12]) m.p. 81-90°C. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.17 - 0.92 (m, 6H), δ 2.24 - 1.68 (m, 8H), δ 2.96 - 2.59 (m, 2H).

cis Dimethyl 1,5-Dimethylbicyclo[3.3.0]octane-3,7-dicarboxylate as a mixture of diastereomers (11)

In a 500 mL boiling flask equipped with a stir bar and a condenser, a solution of 7.68 g (41 mmol) of *cis* 1,5-dimethylbicyclo[3.3.0]octane-3,7-dicarbonitrile dissolved in 55 mL of methanol, a solution of 25.33 g (452 mmol) of KOH dissolved in 90 mL methanol, and 50 mL of water were added. The reaction mixture

was heated to reflux in an oil bath and left overnight. The vessel was then cooled to room temperature and HCl (conc., aq.) was added until pH < 7. Ether and water were added to the resultant slurry to dissolve the solids and then separated. The aqueous layer was extracted with ether, and the combined organics were washed with sat. aq. NaCl, and dried over $MgSO_4$. The solvents were removed under reduced pressure to afford the crude diacid which was treated with diazomethane without further purification (see below). The crude yield was highly variable due the difficulty in removing water and methanol from the diacid. The progress of the reaction was followed by GC-MS (70 eV) m/z = 226, 208, 190, 180, 162, 139, 127, 108, 95, 93, 79, 67, 55, 41 (The molecular ion was frequently absent). IR (KBr): $\nu = 1699\ cm^{-1}$

The crude mixture of diacids was dissolved in 36 mL THF and methylated with diazomethane. Diazomethane was produced in a special distilling apparatus with fire polished joints made specifically for the generation of diazomethane. This apparatus can be purchased from Aldrich and is called a Diazald kit. All the glassware in the following procedure comes from this kit. KOH (3.8304 g, 68.4 mmol) was dissolved in 18 mL of ethanol and 6 mL of water in a 250 mL round bottom equipped with a stir bar. The neck of the flask was fitted with a Claisen head to which an 125 mL addition funnel and a simple distillation apparatus (3-way connector, condenser, and vacuum adaptor) was attached. The THF solution of the crude diacid was placed in a 500 mL round bottom with a stir bar and attached to the vacuum adaptor. An ice bath was used to cool the receiving flask. 'Diazald' (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, 19.812 g, 93 mmol) was dissolved in 120 mL of ether and added to the addition funnel. The ethanolic base was heated to 60°C with an oil bath whereupon the Diazald solution was added dropwise. A yellow ethereal solution of diazomethane was seen to distill into the THF solution of

diacids. The distillation was continued until a persistent yellow color appeared in the receiving flask, whereupon the addition of Diazald was halted and a portion of clean ether was added to the pot to wash residual ethereal solution of diazomethane into the receiving flask. The excess diazomethane was quenched with sat. aq. NH_4Cl. The yellow color disappeared from the receiving flask upon quenching and bubbles were observed. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organics were then washed with sat. aq. NaCl and dried over $MgSO_4$. Volatile organics were removed under reduced pressure to afford 7.44 g (29 mmol) of **11**. (71% yield, lit. yield 73%[12]) m.p. 69 - 74°C. The completion of the reaction is most easily verified via IR (KBr): ν = 1734 cm^{-1}. The crude product was frequently very clean. Recrystalization from hexanes was used to purify the mixture of diesters upon occasion. ^1H NMR ($CDCl_3$, 200 MHz) δ 1.04 - 0.94 (m, 6H), δ 2.17 - 1.57 (m, 8H), δ 2.99 - 2.68 (m, 2H), δ 3.66 (s, 6H).

Dimethyl 3,7-Dimethyltricyclo[3.3.0.$0^{3,7}$]octane-1,5-dicarboxylate (7)

A 100 mL 3-neck round bottom flask equipped with a stir bar and fitted with a pressure equalizing 15 mL addition funnel, a septum, and a tube adaptor connected to the manifold, was evacuated, flame dried, and filled with nitrogen. The apparatus was allowed to cool to room temperature. Diisopropyl amine (0.8 mL, 6 mmol) was injected through the septum. THF (5.0 mL) was then injected. The solution was stirred, and cooled to -78°C. A 25 mL pear shaped flask was fitted with a septum, evacuated, flame dried, and filled with nitrogen. After allowing the flask to cool to room temperature, 4mL (6 mmol) of 1.5M methyl lithium dissolved in ether was injected. An additional 4.6 mL of ether distilled from sodium was injected, and the solution was swirled. The solution was taken up in a 10 mL disposable syringe and injected into the reaction mixture dropwise. The reaction turned opaque white.

Diester **11** (0.605 g, 2.4 mmol) was placed in a 25 mL pear shaped flask, fitted with a septum, evacuated for several minutes, and filled with nitrogen. THF (2mL) was added to the flask and swirled to dissolve the reactant. This solution was then added dropwise to the reaction mixture. Iodine (0.5770 g, 2.3 mmol) was placed in a 25 mL pear shaped flask, fitted with a septum, evacuated for several minutes, and filled with nitrogen. THF (15 mL) was injected into the flask and swirled to dissolve the iodine. This solution was transferred to the addition funnel. Ten minutes after the completion of the addition of **11**, the iodine was added dropwise. The brown color of the iodine dissipated rapidly upon addition. After the addition of iodine was complete, the reaction mixture was allowed to stir at -78°C for 30 minutes. The mixture was then allowed to warm to room temperature and quenched with sat. aq. NH_4Cl. The two layers were separated and the aqueous layer was extracted with 3 x 50 mL portions of ether. The combined organics were washed with sat. aq. NaCl, and dried over $MgSO_4$. Solvents were removed under reduced pressure to afford the crude product. Care must be taken not to allow the removal of solvents continue after dryness is achieved as **7** is readily sublimed.

The product was purified via column chromatography. A 4.5 cm x 11 cm column was packed with 60Å silica gel wetted with 95% benzene / 5% ethyl acetate by volume solution. The silica gel was settled with the aid of mechanical vibration. Fractions were taken at a rate of 30 sec/fraction with a volume of 16 mL/fraction. The product was detected via GC in fractions 26 - 48. The solvents were removed under reduced pressure, again not allowing the removal to continue after dryness, to afford a material which was then recrystalized from hexanes to yield 173.7 mg (0.69 mmol) of pure product (29% yield, lit. yield 38%[12]). m.p. 95 - 97°C ^1H NMR ($CDCl_3$, 200 MHz) δ 1.20 (s, 6H), δ 1.72 (δ, 4H, J = 8.3 Hz), δ 1.95 (d, 4H, J = 8.3 Hz), δ 3.67 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, broad-band decoupled) δ 16.2,

47.9, 51.8, 56.3, 58.1, 173.6 ppm. IR (CH_2Cl_2): 1731.5 cm^{-1}. MS (70 eV) m/z: 221, 190, 153, 133, 121, 105, 93, 91, 77, 59, 41. (The molecular ion was frequently not observed.)

Two common impurities were isolated and characterized. Methyl 1,5-dimethyltricyclo[3.3.$1^{3,7}$.0]nona-9-one-3-carboxylate has the pernicious tendency to coelute with **7** during column chromatography, and has a similar retention time to **7** using a variety of temperature programs for GC. MS (70 eV) m/z: 222, 190, 162, 145, 134, 121, 107, 95, 93, 91, 79, 77, 67, 55, 41. IR (CCl_4): 1744, 1724 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.07 (s, 6H), δ 1.70 (br d, 1H, J = 11.7 Hz), δ 1.85 (d, 2H, J = 11.7 Hz), δ 1.89 (dd, 2H, J = 11.7 Hz, 4.6 Hz), δ 2.04 (s (probably a doublet with the further downfield splitting obscured by acetone), 2H), δ 2.60 (br s, 1H), δ 3.60 (s, 3H). Methyl 7-iodo-1,5-dimethyltricyclo[3.3.$1^{3,7}$.0]nona-9-one-3-carboxylate tends to run in front of **7** during column chromatography, but several minutes behind **7** in GC traces. MS (70 eV) m/z: 348, 221, 189, 161, 133, 119, 105, 91, 77, 59, 41, 39.

3,7-Dimethyltricyclo[3.3.0.$0^{3,7}$]octane-1,5-dicarboxylic acid (12)

In a 25 mL round bottom equipped with a stir bar, 192.7 mg (0.76 mmol) of **7** was dissolved in 4 ml of methanol. KOH (1.98 g, 35 mmol) was dissolved in water and added to the reaction with stirring. A condenser was fitted to the flask, and the reaction was heated to reflux for three hours. The reaction was then cooled to room temperature and HCl (conc.) was added to lower the pH below 7. Water and ether were then added to dissolve all the solids. The layers were separated, and the aqueous layer was extracted with ether. The combined organics were washed with sat. aq. NaCl and dried over $MgSO_4$. The solvents were removed under reduced pressure to afford 170.2 mg (0.76 mmol) (100% yield) of **12**. m.p. 195°C. ^1H

NMR (acetone-d^6, 200 MHz) δ 1.19 (s, 6H), δ 1.71 (d, 4H, J - 10.1 Hz), δ 1.89 (d, 4H, 10.1 Hz). ^{13}C NMR (acetone-d^6, 75 MHz) δ 16.2, 48.1, 56.1, 58.6, 179.9. IR (CH_2Cl_2): 1711 cm^{-1}.

3,7-Dimethyltricyclo[3.3.0.0^{3,7}]octane-1,5-dicarboxylic anhydride (8)

Diacid **12** (60 mg, 0.27 mmol) was dissolved in 2 mL $CHCl_3$ and one drop of pyridine and transferred to a large test tube. Two drops of $SOCl_2$ were added and the reaction was gently shaken for eight minutes. The reaction was then extracted twice with 1 mL portions of 1M $NaHCO_3$, twice with 1mL portions of 1M HCl, washed with 1 mL sat. aq. NaCl, and dried over $MgSO_4$. The filtrate was transferred to a small round bottom and the solvents were removed under reduced pressure to afford 28.1 mg (0.14 mmol) (51% yield) of **8**. m.p. 153-155°C IR (CCl_4): 1855, 1785, cm^{-1}. MS (70 ev) m/z: 178, 162, 147, 134, 120, 119, 105, 91, 77, 39. High resolution FAB MS found: 207.1017 ± .0005 a.m.u. (molecular ion + H^+), calculated 207.1021 a.m.u. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (s, 6H), δ 2.00 (br d, 4H, 7.8 Hz), δ 2.08 (br d, 4H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) 16.8, 52.8, 55.8, 56.1, 173.0.

3,7-Dimethyl-1,5-diiodotricyclo[3.3.0.0^{3,7}]octane (4)

To a 25 mL 2-neck round bottom equipped with a stir bar, 117.3 mg (0.52 mmol) of **12**, 215.2 mg (0.99 mmol) HgO, 125.6 mg (1.04 mmol) $MgSO_4$, and 895.9 mg (3.53 mmol) of iodine were added. CH_2Cl_2 (8 mL) was added dissolving the acid and iodine, and suspending the HgO and the $MgSO_4$. The reaction was stirred, fitted with a condenser, heated to reflux, and irradiated at close range with a 60W tungsten filament. After 4.5 h, the bulb was turned off and the reaction was allowed to cool to room temperature. The reaction was vacuum filtered through

Celite as an aid. The filtrate was then washed with sat. aq. NaS_2O_3, washed with sat. aq. NaCl, and dried over $MgSO_4$. The solvents were removed under reduced pressure to yield a crude product. The material was purified via column chromatography using 60Å silica gel and hexanes as the solvent. 125.4 mg (0.32 mmol) of pure **4** was thus obtained (62% yield). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19 (s, 6H), δ 1,95 (br d, 4H, J = 7.5 Hz), δ 2.20 (br d, 4H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.1, 45.2, 49.0, 65.8. MS (70 ev) m/z: 388, 261, 134, 119, 105, 91, 77, 39.

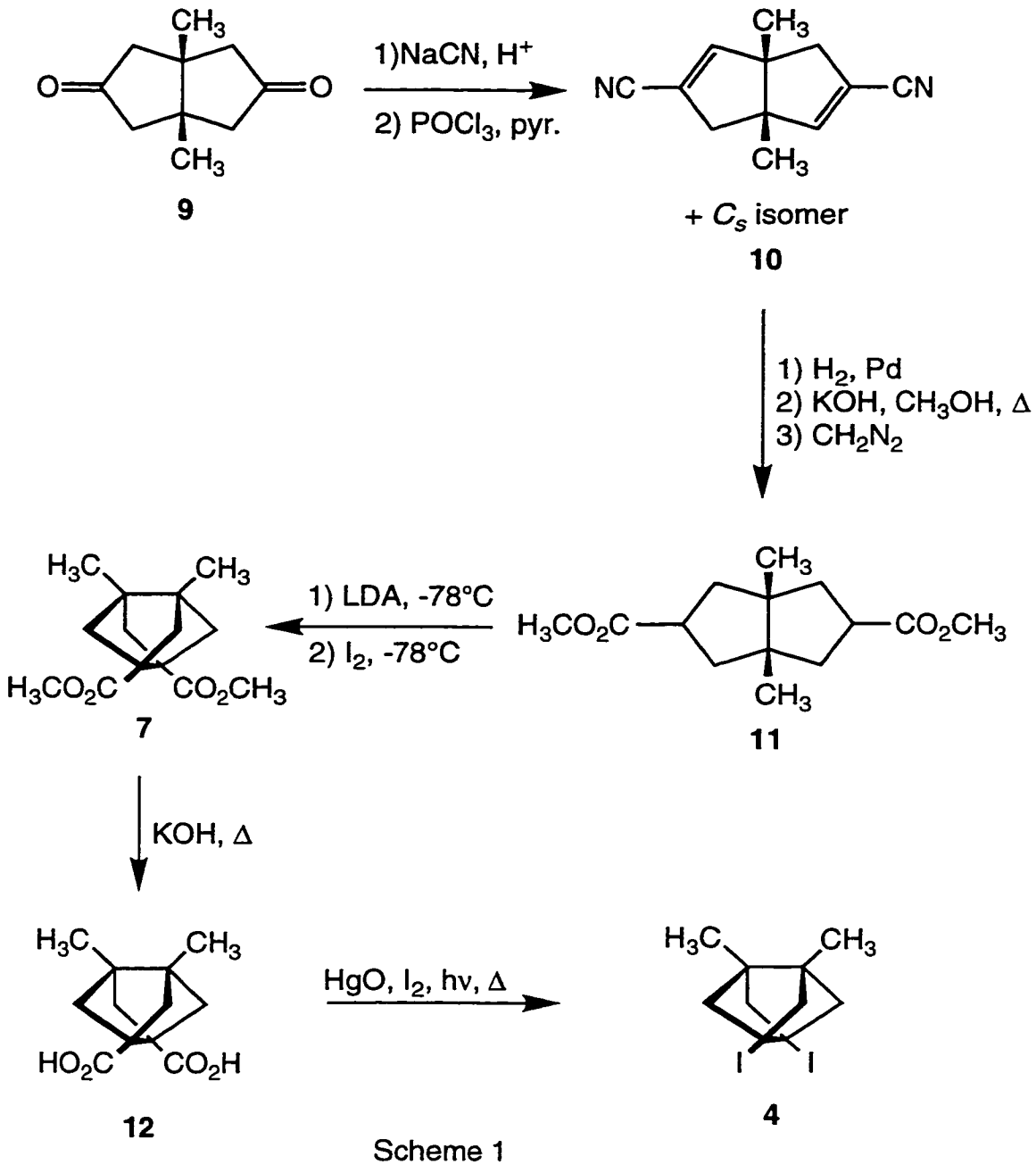


Figure 1.1 Synthetic route to **4**.

Chapter 1 Notes

1. Reviews: (a) Borden, W. T. *Chem. Revs.* **1989**, *89*, 1095. (b) Borden, W. T. *Synlett*, **1996**, *115*, 711.

2. (a) Renzoni, G. E.; Yin, T.-K.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 7121. (b) Branan, B. M.; Paquette, L. A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 774.

3. Smith, J. M.; Hrovat, D. A.; Borden, W. T.; Allan, M.; Asmis, K. R.; Bulliard, C.; Haselbach, E.; Meier, U. C. *J. Am. Chem. Soc.* **1993**, *115*, 3816.

4. Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710.

5. Review: Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127.

6. (a) Kumar, A.; Lichtenhan, J. D.; Critchlow, S. C.; Eichinger, B. E.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 5633. (b) Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 1912. (c) Nicolaides, A.; Smith, J. M.; Kumar, A.; Barnhart, D. M.; Borden, W. T. *Organometallics* **1995**, *14*, 3475.

7. Radziszewski, J. G.; Yin, T.-K.; Renzoni, G. E.; Hrovat, D. A.; Borden, W. T.; Michl, J. *J. Am. Chem. Soc.* **1993**, *115*, 1454.

8. Radziszewski, J. G.; Yin, T.-K.; Miyake, F.; Renzoni, G. E.; Borden, W. T.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3544. Renzoni, G. E.; Yin, T.-K.; Miyake, F.; Borden, W. T. *Tetrahedron* **1986**, *42*, 1581.

9. Allan, M. *J. Electron Spectrosc. Relat. Phenom.* **1989**, *48*, 219. Allan, M. *Helv. Chim. Acta* **1982**, *65*, 2008. Asmis, K. R.; Allan, M. *J. Chem. Phys.* **1997**, *106*, 7044.

10. Bulliard, C.; Allan, M.; Smith, J. M.; Hrovat, D. A.; Borden, W. T.; Grimme, S. *Chem. Phys.* **1997**, *225*, 153.

11. Hoffmann, H. M. R.; El-Khawaga, A. M.; Oehlerking, H.-H.*Chem. Ber.* **1991**, *124*, 2147.

12. Camps, P.; Iglesias, C.; Rodríguez, M. J.; Grancha, M. D.; Gregori, M. E.; Lozano, R.; Mirands, M. A.; Figueredo, M.; Linares, A. *Chem. Ber.* **1988**, *121*, 647.

13. Camps, P.; Font-Bardia, M.; Pérez, F.; Solans, X.; Vásquez, S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 912.

14. Fujimori, K. in "Organic Peroxides"; Ando, W., Ed. John Wiley & Sons: New York, 1992, pp. 319-85.

15. Carpenter, F. H. *J. Am. Chem. Soc.* **1948**, *70*, 2964.

16. Bertz, S. H.; Cook, J. M.; Gawish, A.; Weiss, U.; *Org. Synth.* **1990**, *7*, 50. Weiss, U.; Edwards, J. M. *Tetrahedron Lett.* **1968**, 4885.

Chapter 2:

A Summary of the Theoretical Projects Completed

The following chapters in this thesis describe the results of three very different computational projects, but all of which were concerned with the chemistry of the cyclopropyl group. Chapter 3 investigates the sources of strain in cyclopropane rings containing unsaturated centers. In Chapter 4 calculations are presented on the singlet state of a derivative of the trimethylene diradical which might be stable enough to study spectroscopically. Chapter 5 describes calculations on the stereomutation of some spiropentanes and reinterprets the kinetic data to show that they open in the anticipated conrotatory sense.

Heats of formation show that ca. 14 kcal/mol of additional strain in introduced for each sp^2 center in a cyclopropane ring.[1] The widely accepted explanation is that the angle strain associated with an sp^2 center is much greater than that associated with an sp^3 center. The computational research in Chapter 3 on this subject was inspired by Roth's experimental finding that the barrier to rotation about the π bond in a substituted methylenecyclopropane is only ca. 4 kcal/mol lower than for a typical π bond.[2] If the presence of the π bond caused the additional strain, then the rehybridization of the sp^2 center upon breaking the π bond should alleviate this strain; yet this was not Roth's observation.

The low barrier to inversion of methylcyclopropyl radical also leads one to believe that additional angle strain is not the primary source of the destabilization of methylenecyclopropane and cyclopropene. This barrier, which reflects the extra angle strain involved in planarizing a cyclopropyl carbon, and thus creating an sp^2 center amounts to only ca. 3 kcal/mol.

My calculations confirmed that the increase in strain from introducing an sp^2 carbon into a three membered ring is not due to increased angle strain. Instead, as discussed in detail in the next chapter, I showed that the strain in methylenecyclopropane and in cyclopropene is due to the absence of strong C-H bonds which are present in cyclopropane.

Chapter 4 is concerned with a derivative of the trimethylene diradical, a species which has inspired much research over a span of several decades.[3] Singlet trimethylene can be accessed by cleavage of a bond in a cyclopropane ring; and the preferred mechanism for this reaction -- conrotation, disrotation, or monorotation, -- has been the subject of many calculations and experiments. The ground state of the trimethylene diradical has also been of considerable interest. Calculations indicate that the triplet state is preferred. Closs's experiments have shown that a cyclic derivative of trimethylene does, in fact, have a triplet ground state.[4] However, calculations predict that selective stabilization of the singlet state can be achieved by substituting the central carbon with strong hyperconjugative donors or acceptors.[5] These hyperconjugative interactions can also create pronounced preferences for con- or disrotation.[5] Experiments have found[5e] that, as predicted,[5d] geminal fluorines confer a singlet ground state on a derivative of 2,2-difluorocyclopentane-1,3-diyl and result in a strong preference for disrotatory ring opening in a derivative of 1,1-difluorocyclopropane.

These results caused me to investigate 2,2-disilylcyclopentane-1,3-diyl and its 1,3-divinyl derivative.[6] My calculations found that the central bond in 5,5-disilyl-1,3-divinylbicyclo[2.1.0]pentane has a small but positive BDE, so ring closure of 1,3-divinyl-2,2-disilylcyclopentane-1,3-diyl is predicted to be thermodynamically favorable. However, the electronic preference of this diradical against undergoing

disrotatory ring closure results in my calculations predicting that this reaction should have a high barrier.

Chapter 5 reports a computational study of the potential surface for the opening of spiropentane.[7] If strong hyperconjugative donors like silyl groups can stabilize a 1,3-diradical, and lead to a large preference for conrotatory ring closure, one might expect a cyclopropane group to do the same. The stereomutations of spiropentanes were studied experimentally nearly twenty years ago, but a large preference for conrotation was not found.[8] In fact, the experimental results were interpreted in terms of a small preference for disrotation over both conrotation and monorotation. Nevertheless, my calculations found conrotation to be preferred to both disrotation and monorotation. Further, our calculations showed that the resolution of the apparent conflict between theory and experiment is that the experimental data was misinterpreted, due to an erroneous assumption made in analyzing the data. My computational results revealed that a novel long-range nonbonded attraction contributes to rendering this assumption incorrect.

The three chapters that follow are taken almost directly from the publications which describe the theoretical projects that I completed as part of the research for this dissertation. Therefore, each of the chapters has its own set of references, even though some of the literature cited is common to all three chapters.

Chapter 2 Notes

1. Johnson, W. T. G.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 5930.

2. Roth, W. R.; Quast, M. unpublished results.

3. Getty, S. J.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2085; Baldwin, J. E.; Yamaguchi, Y.; Schaefer, H. F., III *J. Phys. Chem.* **1994**, *98*, 7513; Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc*, **1997**, *119*, 5251. Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc*, **1997**, *119*, 5253. References to earlier *ab initio* calculations and to experimental studies of cyclopropane stereomutations are contained in these four papers.

4. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

5. (a) Skancke, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 7079; (b) Getty, S. J.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, **1994**, *116*, 1521; (c) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc. Faraday Trans.* **1994**, *90,* 1689; (d) Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, **1994**, *116*, 5425; (e) Tian, F.; Lewis, S. B.; Bartberger, M. D.; Dolbier, W. R., Jr.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 6187.

6. Johnson, W. T. G.; Hrovat, D. A.; Skancke, A.; Borden, W. T. *Theor. Chem. Acc.* **1999**, *102*, 207.

7. Johnson, W. T. G.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* (accepted for publication).

8. Gilbert, J. C. *Tetrahedron* **1969**, *25*, 1459; Gajewski, J. J.; Burka, L. T. *J. Am. Chem. Soc.* **1972**, *94*, 8857; Gajewski, J. J. *Chem. Commun.* **1967**, 920; Gajewski, J. J. *J. Am. Chem. Soc.* **1970**, *92* , 3688; Gajewski, J. J.; Chang, M. J. *J.*

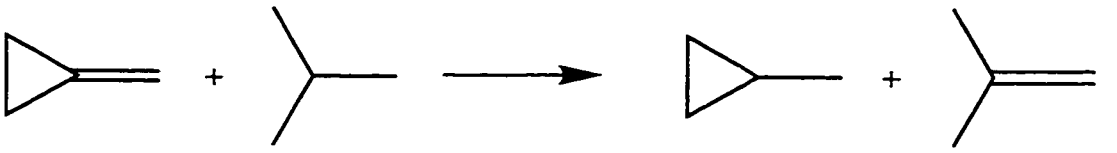
Am. Chem. Soc. **1980**, *102*, 7542; Gajewski, J. J.; Weber, R. J.; Chang, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2100.

Chapter 3:

Why Are Methylenecyclopropane and Cyclopropene More Strained than Cyclopropane?

In 1968, Wiberg and Fenoglio measured the heats of formation of methylenecyclopropane and 1-methylcyclopropene.[1] From their measurements they concluded that introduction of each trigonal center into a cyclopropane ring results in an increase in strain energy of 12 - 14 kcal/mol.

For example, using Wiberg and Fenoglio's value for the heat of formation of methylenecyclopropane[2] and literature values for the heats of formation of methylcyclopropane,[2,3] isobutylene,[3] and isobutane,[3] the isodesmic reaction in eq 1 is found to be exothermic by 14.3 kcal/mol. Eq 1 can either be construed as measuring the difference between the heats of hydrogenation of methylenecyclopropane and isobutylene or the difference between the energies required to convert isobutane and isobutylene into, respectively, methylcyclopropane and methylenecyclopropane. Both interpretations of eq 1 indicate that methylenecyclopropane is ca. 14 kcal/mol more strained than methylcyclopropane.



(1)

Quite reasonably, Wiberg and Fenoglio attributed the greater strain energies of methylenecyclopropane and 1-methylcyclopropene to the additional angle strain that results from the presence of, respectively, one and two nominally sp^2, rather

than sp^3, carbons in a three-membered ring.[1] This explanation seems to have been widely accepted.[4]

Upon breaking the π bond in methylenecyclopropane, the trigonal ring carbon can pyramidalize, thus relieving the additional angle strain that results from the presence in the three-membered ring of a carbon that is nominally sp^2, rather than sp^3, hybridized. The strain released upon pyramidalization of the trigonal carbon in the transition state should be reflected in an unusually low barrier to rotation about the double bond in methylenecyclopropane.[5] However, Roth and coworkers have recently found that the barrier to rotation about the double bond in a methylenecyclopropane derivative is only 3.7 kcal/mol less than the rotational barrier in a similarly substituted isobutylene derivative.[6] This very modest lowering of the rotational barrier is only a small fraction of Wiberg and Fenoglio's value of 14 kcal/mol for the additional strain energy in methylenecyclopropane, compared to cyclopropane.

Methodology

In order to reconcile these apparently conflicting experimental results, I performed *ab initio* calculations, using the 6-31G* basis set.[7] Geometries were optimized and vibrational frequencies computed using (2,2)CASSCF for alkenes and diradicals, ROHF for radicals, and RHF for alkanes. These calculations were performed with the Gaussian 94 suite of programs.[8]

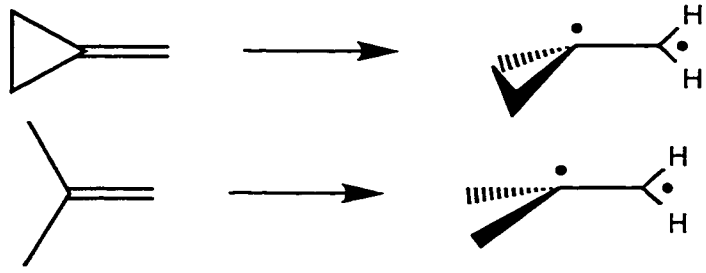
Single-point energies for alkanes were recalculated at the MP2 level,[9] using Gaussian 94. For single-point calculations on alkenes, radicals, and diradicals the CASPT2N method[10] was employed. For single-point calculations on radicals the ROMP2 method was employed. The CASPT2N and ROMP2 calculations were

carried out with MOLCAS.[11] The calculated electronic energies and the vibrational corrections to them are given in Table 3.1.

The Extra Strain in Methylenecyclopropanes

Using the data in Table 3.1, we computed $D\mathit{H}^{298}$ for the isodesmic reaction in eq 1. After correcting the electronic energies for zero-point energies and heat capacities, $D\mathit{H}^{298}$ = -12.2 kcal/mol was obtained at the CASSCF-RHF level of theory, and -11.7 kcal/mol was computed at CASPT2N-MP2. Given the sizes of the uncertainties in the experimental heats of formation of the four hydrocarbons in eq 1,[2-4] the agreement between the experimental value of $D\mathit{H}^{298}$ = -14.3 kcal/mol and these calculated values is satisfactory.

Next we compared the barrier to rotation about the double bond in methylenecyclopropane (eq 2) with that in isobutylene (eq 3). For the former reaction $D\mathit{H}^{\ddagger}$ = 58.9 and 57.2 kcal/mol were calculated at, respectively, the CASSCF and CASPT2N levels of theory. For the latter reaction these values were $D\mathit{H}^{\ddagger}$ = 63.1 and 61.6 kcal/mol. In agreement with the experimental results of Roth and coworkers,[6] the barrier to rotation in methylenecyclopropane is calculated to be lower than that in isobutylene by ca. 4 kcal/mol, but this difference between the calculated barrier heights is only a third of the 12 kcal/mol difference between the calculated heats of hydrogenation.

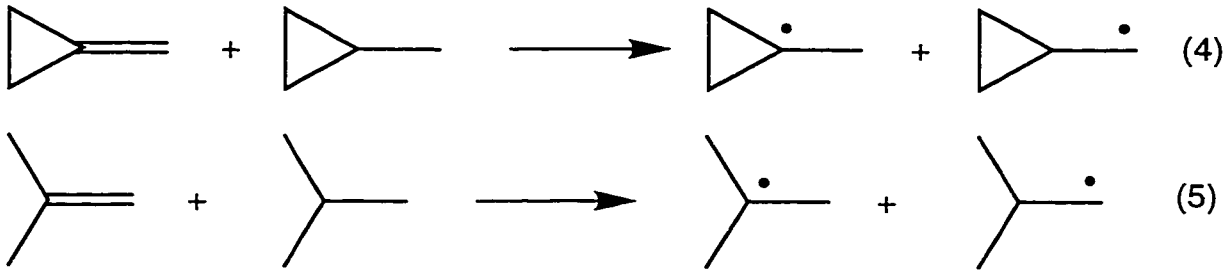


(2)

(3)

By constraining to planarity the tertiary radical center in each of the two transition states, the contribution of relief of angle strain to the lower value of D*H*‡ for rotation about the double bond in methylenecyclopropane can be evaluated.[5] At the CASSCF level of theory the resulting increase in the energy of the transition state is 4.6 kcal/mol for methylenecyclopropane but only 1.1 kcal/mol for rotated isobutylene. The CASPT2N transition state energy increases are, respectively, 1.8 and 0.3 kcal/mol. Thus, only 1.5 - 3.5 kcal/mol of the 4.3 kcal/mol difference between the rotational barriers is due to selective relief of angle strain on pyramidalization of the tertiary radical center in the transition state for rotation about the double bond in methylenecyclopropane. The balance of the 4.3 kcal/mol difference between the two rotational barriers can be attributed (*vide infra*) to selective stabilization of the primary radical center by the bent bonds of the adjacent cyclopropyl ring in this transition state.[12]

An analysis that uses Benson's "thermodynamic" definition of π BDEs,[13] rather than the "kinetic" definition based on rotational barriers, also shows that relief of angle strain makes only a minor contribution to the exothermicity of the isodesmic reaction in eq 1. The thermodynamic π BDEs of methylenecyclopropane and isobutylene are given, respectively, by the enthalpies of the reactions in eqs 4 and 5.



(4)

(5)

Using these definitions, the π BDE at 298 K of methylenecyclopropane is calculated to be 57.9 kcal/mol at the CASSCF-RHF-ROHF level of theory and 58.0

kcal/mol when correlation is included at the CASPT2N-MP2-ROMP2 level of theory. The corresponding π BDEs for isobutylene are, respectively, 62.8 and 63.4 kcal/mol. The CASSCF-RHF-ROHF and CASPT2N-MP2-ROMP2 differences between the thermodynamic π BDEs of methylenecyclopropane and isobuylene (eqs 4 and 5) are thus, respectively, 4.9 and 5.4 kcal/mol. These values are close to but are slightly larger than the ca. 4.3 kcal/mol difference between the kinetic π BDEs (eqs 2 and 3) that is computed at both the CASSCF and CASPT2N levels of theory.

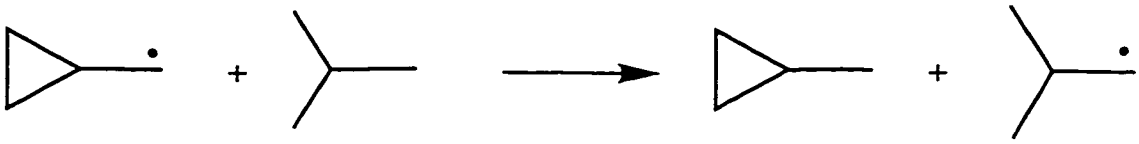
One contributor to the difference between the thermodynamic π BDEs of methylenecyclopropane and isobutylene is the greater stabilization on pyramidalization of 1-methylcyclopropyl radical than of *tert*-butyl radical. At the ROHF and ROMP2 levels of theory these pyramidalization energies are, respectively, 6.1 and 3.8 kcal/mol for the former radical and 2.1 kcal/mol and 1.4 kcal/mol for the latter.[14,15] Thus, the difference in pyramidalization energies between the two tertiary radicals in eqs 4 and 5 accounts for only 2.4 - 4.0 kcal/mol of the 4.9 - 5.5 kcal/mol difference between the thermodynamic π BDEs of methylenecyclopropane and isobutylene.

Most of the remainder of the difference between the thermodynamic π BDEs of these two alkenes can be accounted for by stabilization of the radical center in cyclopropylmethyl radical by the bent bonds of the adjacent cyclopropane ring.[16] For example, the "bisected" conformation of cyclopropylmethyl radical, which provides the best overlap between the ring bonds and the singly occupied AO of the CH_2 group, is lower in energy than the C_s "staggered" conformation by 0.9 kcal/mol at the ROHF level and by 2.2 kcal/mol at the ROMP2 level of theory.

Obviously, the difference between the heats of hydrogenation of methylenecyclopropane and isobutylene in eq 1 does not reside principally in a

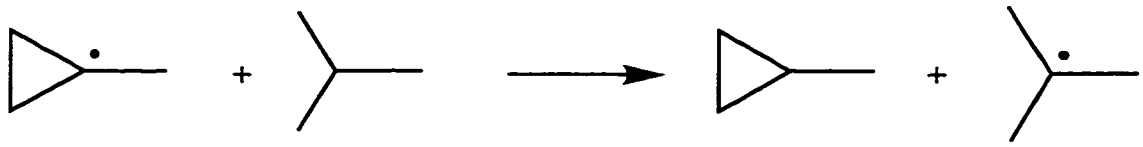
reduction, due to relief of angle strain, in the strength of the π bond that is broken upon hydrogenation of methylenecyclopropane. Therefore, the exothermicity of the reaction in eq 1 must be due to formation of a particularly strong C-H bond when methylenecyclopropane is hydrogenated. Indeed, our calculations show this to be the case.

The difference between the strengths of the primary C-H bonds formed in the hydrogenation of methylenecyclopropane and of isobutylene is given by the isodesmic reaction in eq 6. The reaction in eq 6 is calculated to be endothermic by 1.4 kcal/mol at the ROHF-RHF level and by 2.8 kcal/mol when electron correlation is included at the ROMP2-MP2 level. The lower primary C-H BDE in methylcyclopropane than in isobutane can again be attributed to the selective stabilization of the radical center in cyclopropylmethyl radical by the bent bonds of the adjacent cyclopropyl group.[16]



(6)

The difference between the strengths of the tertiary C-H bonds formed in the hydrogenation of methylenecyclopropane and of isobutylene is given by the isodesmic reaction in eq 7. In contrast to the small endothermicity calculated for the reaction in eq 6, the reaction in eq 7 is computed to be highly exothermic, by -8.6 kcal/mol at ROHF-RHF and by -9.1 kcal/mol with inclusion of correlation at the ROMP2-MP2 level. The exothermicity of this reaction reflects the unusually strong C-H bonds formed by the cyclopropyl ring carbons.[17] Thus, our calculations show that the biggest contributor to making the heat of hydrogenation of methylenecyclopropane considerably larger than that of isobutylene is the greater strength of the tertiary C-H bond in methylcyclopropane than in isobutane.



(7)

As noted above, the reaction in eq 1 can be viewed as comparing, instead of the heats of hydrogenation of methylenecyclopropane and isobutylene, the energies required to convert isobutane and isobutylene into, respectively, methylcyclopropane and methylenecyclopropane. From the latter perspective the major contributor to making methylcyclopropane easier to form than methylenecyclopropane is the presence of a tertiary C-H bond in isobutane, which is absent in isobutylene. Our calculations find that this C-H bond is strengthened by ca. 9 kcal/mol on conversion of isobutane to methylcyclopropane. Thus, our calculations show that most of the additional "strain" energy in methylenecyclopropane, relative to methylcyclopropane, resides, not in angle strain, but in the tertiary C-H bond that is present in methylcyclopropane but absent in methylenecyclopropane.[18]

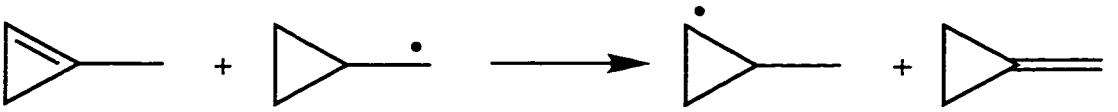
The Extra Strain in Cyclopropenes

Our calculations find that the major portion of the higher heat of formation of 1-methylcyclopropene, compared to methylenecyclopropane, has a similar origin. The measurements of Wiberg and Fenoglio yielded a difference in heat of formation of 10.2 kcal/mol between these two isomers.[2] In reasonable agreement with this experimental value, we calculate 1-methylcyclopropene to have the higher heat of formation by 12.7 kcal/mol at the CASSCF level and by 11.2 kcal/mol at CASPT2N.

Because 1-methylcyclopropene and methylenecyclopropane are isomers, the difference between their heats of formation is equal to the difference between

their heats of hydrogenation. By calculating the differences between the energies of the π bonds that are broken and the C-H bonds that are made in the hydrogenation of both compounds, the origin of the difference in heats of formation can be established.[19]

The structural relationship between 1-methylcyclopropene and methylenecyclopropane results in the difference between their thermodynamic π BDEs reducing to the enthalpy of the isodesmic reaction in eq 8. This reaction is calculated to be exothermic by 4.8 and 2.4 kcal/mol at, respectively, the CASSCF-ROHF and CASPT2N-ROMP2 levels of theory. Pyramidalization of the secondary radical center in 2-methylcyclopropyl radical is calculated to lower selectively the π BDE of 1-methylcyclopropene by 3.7 kcal/mol at the RHF level but by only at 1.8 kcal/mol at ROMP2.[16] Thus, the differences in angle strain are obviously not responsible for the bulk of the ca. 10 kcal/mol difference between the heats of formation of 1-methylcyclopropene and methylenecyclopropane.



(8)

Since the difference in π BDEs accounts for only a small part of the difference between the heats of formation of these two isomers, the bulk of the difference in their heats of formation must reside in a difference in C-H bond strengths. The latter difference can easily be shown to be equal to the difference between the heats of formation of 2-methylcyclopropyl radical and cyclopropylmethyl radical. We calculate this difference to be 7.9 and 8.8 kcal/mol at, respectively the ROHF and ROMP2 levels of theory.

The difference between the heats of formation of these two radicals is equal to the difference between the BDEs of a secondary and a primary C-H bond in

methylcyclopropane. Therefore, the major reason why 1-methylcyclopropene has a higher heat of formation than methylenecyclopropane is that a secondary cyclopropyl C-H bond in the latter alkene is considerably stronger than a primary methyl C-H bond in the former.

Conclusions

In summary, our calculations find that, as suggested by Wiberg and Fenoglio,[1] introduction of a trigonal center into a three-membered ring does, indeed, create some additional angle strain. However, our computational results show that the major source of the additional "strain" that results from the introduction of each trigonal center into a cyclopropane ring is not an increase in angle strain but the loss of a very strong cyclopropane C-H bond.

Table 3.1: Calculated Energetics for Structures in Chapter Three. SCF, MP2, and Zero-Point Energies and Heat Capacities

Molecule	SCF (hartrees)[a]	MP2 (hartrees)[b]	ZPE (kcal/mol)	C_V^{298} (cal/mol-K)
Methylenecyclopropane	-154.9148	-155.4185	57.0	14.0
Methylcyclopropane	-156.0959	-156.6363	73.7	15.0
Methylenecyclopropane TS[c]	-154.8167	-155.3231	54.1	14.8
'Planar' Methylenecyclopropane TS[d]	-154.8094	-155.3203	53.5	13.1
1-Methylcyclopropyl Radical	-155.4543	-155.9757	64.6	15.1
Planar 1-Methylcyclopropyl Radical	-155.4446	-155.9697	63.7	13.7
Bisected Cyclopropylmethyl Radical	-155.4616	-155.9841	63.9	15.9
Cs Staggered Cyclopropylmethyl Radical	-155.4601	-155.9806	63.7	15.9
Isobutylene	-156.1378	-156.6486	72.0	17.5
Isobutane	-157.2990	-157.8472	88.3	18.8
Isobutylene TS[c]	-156.0323	-156.5456	68.5	18.9
Planar Isobutylene TS[d]	-156.0305	-156.5452	67.7	17.4
tert-Butyl Radical	-156.6707	-157.2007	78.8	19.3
Planar C_S *tert*-Butyl Radical	-156.6673	-157.1985	78.0	17.9
C_S Bisected Isobutyl Radical	-156.6613	-157.1904	77.8	18.5
C_S Staggered Isobutyl Radical	-156.6625	-157.1905	78.5	19.6
1-Methylcyclopropene	-154.8943	-155.4004	56.5	15.1
trans-2-Methylcyclopropyl Radical	-155.4494	-155.9701	64.5	15.0
cis-2-Methylcyclopropyl Radical	-155.4496	-155.9706	64.5	15.0
Planar 2-Methylcyclopropyl Radical	-155.4414	-155.9655	63.3	14.3

[a] RHF for alkanes, ROHF for radicals, and (2/2)CASSCF for diradicals and alkenes. [b] MP2 for alkanes, ROMP2 for radicals, and CASPT2 for diradicals and alkenes. [c] Transition state for π bond rotation. [d] Transition state for π bond rotation with the tertiary radical center constrained to planarity.

Chapter 3 Notes

1. Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

2. Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman & Hall, New York, 1986.

3. Kolesov, V. P., and Kozina, M. P. *Russ. Chem. Rev.*, **1986**, *55*, 912.

4. See, for example, Liebman, J. F.; Greenberg, A.; *Chem. Rev.*, **1976**, *76*, 311, p. 324; Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*, Academic Press, New York, 1978, pp. 91-3; Halton, B.; Banwell, M. G. in "The Chemistry of the Cyclopropyl Group", Rappoport, Z., Ed., John Wiley & Sons: New York, 1987, Vol. 1, Part 2, p. 1251.

5. For examples see: Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109,* 5275; Hrovat, D. A.; Sun, H.; Borden, W. T. *Theochem* **1988**, *163*, 51; Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111,* 7282; Hammons, J. H.; Coolidge, M. B.; Borden, W. T. *J. Phys. Chem.* **1990**, *94*, 5468; Coolidge, M. B.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114,* 2354; Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114,* 8682.

6. Roth, W. R.; Quast, M. unpublished results.

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

8. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian 94, Revision B.3, Gaussian, Inc., Pittsburgh PA, 1995.

9. Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618; Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *S10*, 1.

10. Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483; Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

11. Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O., MOLCAS-3, University of Lund, Sweden.

12. The amount by which (2,2)CASSCF overestimates the barrier to planarity at the tertiary radical center, relative to CASPT2N, is fortuitously nearly the same as the amount by which (2,2)CASSCF underestimates the stabilizing interaction between the primary radical center and the bent bonds of the cyclopropane ring. However, since CASPT2N uses second-order perturbation theory, it tends to overestimate the effects of dynamic correlation. Inclusion of these effects variationally would be expected to yield results that are bracketed by the CASSCF and CASPT2N values but which are closer to the latter.

13. Benson, S. W. *J. Chem. Ed.* **1965**, *42*, 502; Benson, S. W.; "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; pp 63-65.

14. After correcting for differences in zero-point energies and heat capacities, our calculations predict $\Delta H^{\ddagger} = 3.3$ kcal/mol for inversion in the 1-methylcyclopropyl radical at 298K. This calculated value is in excellent agreement with the experimental value of $E_a = 3.1 \pm 0.2$ kcal/mol obtained by an EPR study of the rate of inversion of this radical in the temperature range 92-161 K. Deycard, S.; Hughes, L.; Lusztsyk, J.; and Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 4954.

15. For other *ab initio* calculations of barriers to inversion in cyclopropyl radicals see, *inter alia*: Apeloig, Y.: Nakash, M. *J. Am. Chem. Soc.* **1994**, *116*, 10781.

Barone, V.; Minichino, C.; Faucher, H.; Subra, R.; Grand, A. *Chem. Phys. Lett.* **1993**, *205*, 324. Lien, M. H.; Hopkinson, A. C. *J. Comput. Chem.* **1985**, *6*, 274.

16. McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1971**, *3*, 359; Danen, W. C., *J. Am. Chem. Soc.* **1972**, *94*, 4835. Radom, L; Paviot, J.; Pople, J. A.; Schleyer, P. v. R. *J. C. S., Chem. Comm.* **1974**, 58. Walton, J. C., *Magn. Reson. Chem.* **1987**, *25*, 998; Hehre, W. J., *J. Am. Chem. Soc.* **1973**, *95*, 2643.

17. The C-H BDE in cyclopropane at 298 K has been measured to be 106.3 ± 0.3 kcal/mol (Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101,* 2838), which is nearly 8 kcal/mol larger than the BDE at 298 K of 98.6 ± 0.4 kcal/mol for a secondary C-H bond in propane (Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D; Kransoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847). Of the several reasons considered by Baghal-Vayjooee and Benson for the unusually high C-H BDE in cyclopropane, the major cause, indicated by our calculations, is not a large increase in strain on forming a planar cyclopropyl radical but the unusually large amount of carbon 2s character in a cyclopropane C-H bond.

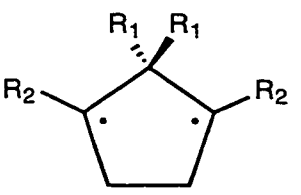
18. It has previously been noted that the strong C-H bonds in cyclopropane reduce its apparent strain energy. Hamilton, J. G.; Palke, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 4159.

19. Calculating these differences in BDEs is the same as calculating separately the changes that occur in the energies of the π C-C and σ C-H bonds in converting one isomer into the other.

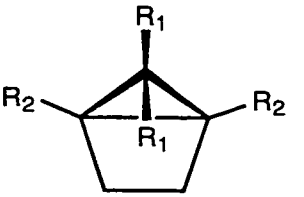
Chapter 4:

Ab Initio Calculations Find 2,2-Disilylcyclopentane-1,3-diyl Is a Singlet Diradical with a High Barrier to Ring Closure

In 1975 Buchwalter and Closs observed the triplet EPR spectrum of cyclopentane-1,3-diyl (**1**).[1] In agreement with the results of this experiment, *ab initio* calculations by Conrad, Pitzer, and Schaefer found the triplet to lie below the singlet by 0.9 kcal/mol.[2] Subsequent CISD(Q) calculations by Sherrill, Seidl, and Schaefer obtained a value of 1.3 kcal/mol for the barrier to ring closure of singlet **1** to bicyclo[2.1.0]pentane (**5**).[3] The calculated size of this barrier is in good agreement with the experimental estimate of Herman and Goodman.[4]



1, $R_1 = H$, $R_2 = H$
2, $R_1 = F$, $R_2 = H$
3, $R_1 = SiH_3$, $R_2 = H$
4, $R_1 = SiH_3$, $R_2 = CH{=}CH_2$



5, $R_1 = H$, $R_2 = H$
6, $R_1 = F$, $R_2 = H$
7, $R_1 = SiH_3$, $R_2 = H$
8, $R_1 = SiH_3$, $R_2 = CH{=}CH_2$

A triplet ground state has also been predicted computationally for the (0,0) conformation of the trimethylene diradical (propane-1,3-diyl),[5] of which **1** is a derivative. However, substitution of geminal fluorines at C-2 of trimethylene and at C-2 of **1** has been predicted to result in a singlet ground state for both 2,2-difluorotrimethylene[6] and for 2,2-difluorocyclopentane-1,3-diyl (**2**).[7] In both of these fluorinated diradicals the low lying σ^* C-F orbitals at C-2 stabilize the in-phase combination of p-π orbitals at C-1 and C-3, relative to the out-of-phase combination, which has a node at C-2. This selective stabilization of one of the nonbonding MOs

is sufficiently large in **2** to result in the singlet's being computed to fall below the triplet in energy by ΔE_{S-T} = -10.0 kcal/mol at the CASPT2 level of theory.[7]

Because the in-phase combination of p-π orbitals at C-1 and C-3 is selectively occupied in the lowest singlet state of **2**, this diradical is predicted to close to 5,5-difluorobicyclo[2.1.0]pentane (**6**) without a barrier; so **2** is the transition state for ring inversion of **6**. The direct observation of **2** and, hence, experimental confirmation of the prediction of a singlet ground state for this diradical is, consequently, expected to be difficult. However, substitution of phenyl groups at C-1 and C-3 has been found to provide sufficient kinetic stabilization for a derivative of **2** to allow its observation.[8] The absence of an EPR signal, the kinetics of disappearance, and the failure to observe trapping by oxygen all point to a singlet ground state for this 1,3-diphenyl derivative of diradical **2**.

2,2-Disilyltrimethylene has also been predicted to be a ground state singlet by recent *ab initio* calculations.[9] In this diradical the high lying C-Si σ orbitals donate electron density into the in-phase combination of p-π orbitals at C-1 and C-3, thus destabilizing this nonbonding orbital and leading to the selective occupancy of the out-of-phase combination of p-π orbitals in the lowest singlet state. The same type of strong hyperconjugative electron donation from C-Si bonds should also be present in 2,2-disilylcyclopentane-1,3-diyl (**3**) and should make this diradical a ground state singlet too.

I performed *ab initio* calculations in order to verify that the singlet is computed to lie below the triplet in **3** and to predict the size of the singlet-triplet energy gap. Additionally, **3** is expected to have a barrier to ring closure, because, unlike the case in **2**, the out-of-phase combination of p-π orbitals at C-1 and C-3 should be selectively occupied in the lowest singlet state of **3**. A sufficiently high barrier to ring

closure to 5,5-disilylbicyclo[2.1.0]pentane (**7**) could render **3** kinetically stable at low temperatures; so calculating the height of this barrier was of considerable interest.

The dissociation energy of the C-1 - C-4 bond in **7** is expected to be unusually low. Strain relief makes the energy difference between cyclopentane-1,3-diyl (**1**) and bicyclo[2.1.0]pentane (**5**) less than 36 kcal/mol,[3,7,10] and stabilization of diradical **3** by hyperconjugative electron donation from the C-Si bonds should make the energy difference between **3** and **7** significantly smaller.

Benzylic stabilization of both radical centers in **1** lowers the barrier to ring inversion of 1,4-diphenylbicyclo[2.1.0]pentane to only 12 kcal/mol;[11] and a sufficiently high degree of hyperconjugative stabilization of singlet **3** might render its 1,3-diphenyl derivative lower in energy than the corresponding ring-closed product. Since the allylic stabilization energy is known to be only 1 - 2 kcal/mol larger than the benzylic stabilization energy,[12,13] rather than performing calculations on the diphenyl derivatives of **3** and **7**, we chose, instead, to carry out calculations on the divinyl derivatives, **4** and **8**.

Herein we report the results of our *ab initio* calculations on the singlet-triplet energy differences in diradicals **3** and **4**, the heights of their barriers to ring closure, and the energies of these diradicals relative to the corresponding bicyclopentanes, **7** and **8**, respectively.

Methodology

Calculations were performed with the 6-31G* basis set.[14] The geometry of triplet **3** was optimized using an ROHF wavefunction. TCSCF wavefunctions were used to optimize the geometries of singlets **3** and **7**. The geometries of the divinyl derivatives **4** and **8** were optimized using (6/6)CASSCF wavefunctions. All of the

geometry optimizations and the subsequent vibrational analyses were performed with Gaussian 94.[15]

The effects of including dynamic electron correlation[16] were investigated by performing CASPT2 calculations,[17] for which the ROHF, TCSCF, and (6/6)CASSCF wavefunctions were used as the references. The CASPT2 calculations were carried out with the MOLCAS suite of *ab initio* programs.[18]

Results and Discussion

Vibrational analyses found the optimized C_{2v} geometries of the singlet and the triplet states of **3** each to have two imaginary frequencies. For each state, one of the modes with an imaginary frequency preserves The C_2 symmetry, and the other preserves C_s symmetry. C_2 and C_s geometries were both optimized for each state, and vibrational analyses showed that the C_2 structures are minima and the C_s structures are transition states, connecting mirror-image C_2 minima. One of the C_2 minima is shown in Figure 4.1.

The geometry for **7** was optimized with C_s symmetry; but a vibrational analysis found this geometry to have one imaginary frequency, corresponding to rotation of the *endo* silyl group. Following this mode led to an optimized C_1 structure, which a vibrational analysis confirmed was an energy minimum. The TCSCF, ROHF, and CASPT2 energies of the stationary points on the singlet and triplet potential surfaces for **3** are given in Table 4.1. The C_2 structures have an advantage over the C_s and C_{2v} structures for both the singlet and triplet, because, as shown in Figure 4.1, in the C_2 structures the C-H bonds at C-4 and C-5 can be staggered; whereas, in the C_s and C_{2v} structures these C-H bonds must be pairwise eclipsed.

In addition, *anti* pyramidalization of C-1 and C-3 minimizes the interaction between the nonbonding AOs at these two carbons. This interaction is slightly

antibonding in the triplet, where the nonbonding MOs are each occupied by one electron, but much more so in the singlet, where the nonbonding MO in which these two AOs are out-of-phase has more than double the occupation number of the MO in which these two AOs are in-phase (1.37 versus 0.63 in the TCSCF wavefunction for $^1A_1$).

Both the greater antibonding interaction between the p-π AOs at C-1 and C-3 and the larger electron density in these AOs in the singlet than in the triplet probably contribute in the singlet having the larger pyramidalization angle at these carbons by 6.1°. As in 2,2-disilylpropane-1,3-diyl,[9] the larger C-1 - C-2 - C-3 bond angle in the C_{2v} singlet (105.2°) than in the C_{2v} triplet (102.1°) also reflects the differing degree to which the interaction between the p-π AOs on these two carbons is antibonding in these two states.

At the CASPT2 level the advantages of pyramidalization at C-1 and C-3 is compensated for, partially in the singlet and fully in the triplet, by the fact that the planar C_{2v} geometry allows more hyperconjugative electron delocalization from the C-Si σ bonds at C-2 into the in-phase combination of the p-π AOs at C-1 and C-3. Delocalization is generally favored by increasing the amount of dynamic electron correlation in the calculation.[16]

The C_2 singlet is 2.9 kcal/mol below the C_2 triplet at the TCSCF-ROHF level and 5.8 kcal/mol below it at the CASPT2 level. As discussed in the introduction, the singlet lies below the triplet because hyperconjugative electron donation from the silyl groups destabilizes the in-phase combination of p-π orbitals sufficiently that selective occupancy of the lower-lying, out-of-phase combination in the singlet overcomes the lower electron repulsion energy in the triplet. The increase in the size of the singlet-triplet energy difference upon inclusion of dynamic electron correlation is

consistent with greater delocalization of the electrons in the C-Si σ bonds in the singlet state than in the triplet.[16]

The selective stabilization of the singlet, relative to the triplet, by hyperconjugation is evident in comparison of the C_{2v} geometries of the two states. In the singlet the bond length of 1.491Å between C-1 and C-2 is 0.020Å shorter than in the triplet; and, as already noted, the 3.1° larger C-1 -C-2 - C-3 bond angle in the singlet also reflects the larger amount of electron delocalization from the C-Si σ bonds in the singlet than in the triplet state.

The presence of the five-membered ring in **3** constrains the C-1 -C-2 - C-3 bond angle to be fully 15.2° smaller in $^1A_1$ than the corresponding bond angle in the (0,0) conformation of singlet 2,2-disilyltrimethylene.[9] The smaller distance between C-1 and C-3 in **3** results in a stronger antibonding interaction between these two carbons in the lowest singlet state of the cyclic, than of the acyclic diradical.

In order to assess the extent to which this antibonding interaction contributes to the calculated reduction in the singlet-triplet gap in the cyclic diradical, we constrained the C-1 - C-2 - C-3 angle in the $^1A_1$ and $^3B_2$ states of 2,2-disilyltrimethylene to be the same as in the corresponding states of **3**. The resulting decrease in this angle of 15.2° in the singlet is 6.1° larger than in the triplet; so it is not at all surprising that the computed singlet-triplet splittings of -3.6 kcal/mol at the TCSCF/ROHF level and -6.1 kcal/mol at the CASPT2 level for constrained 2,2-disilyltrimethylene are much smaller in magnitude than at the unconstrained geometries. The latter values are -6.2 and -11.9 kcal/mol, respectively.[9]

The singlet-triplet splittings, computed at the geometries of 2,2-disilyl-trimethylene that are constrained to have the same C-1 - C-2 - C-3 bond angles as the $^1A_1$ and $^3B_2$ states of **3**, are slightly larger in magnitude than the corresponding values of -1.7 and -4.7 kcal/mol at the optimized C_{2v} geometries of both states of **3**

(Table 4.1). Hyperconjugative electron donation from the C-H bonds of the ethano bridge in the cyclic diradical competes with donation from the C-Si bonds and destabilizes the singlet relative to the triplet, thus reducing the magnitude of the singlet-triplet gap by 1.9 kcal/mol at the TCSCF-ROHF level and by 1.4 kcal/mol at the CASPT2 level. Alkyl substituents at C-1 and C-3 have also been found to destabilize the $^1A_1$ state of unsubstituted trimethylene.[6]

Unlike both **1**[3,4] and **2**,[7] **3** should have a large barrier to ring closure. In **3** the nonbonding MO in which the AOs at C-1 and C-3 are out-of-phase has a much higher occupation number than in **1** or **2**. This should result in closure to the corresponding bicyclo[2.1.0]pentane, which is geometrically constrained to be disrotatory, being much more highly forbidden by orbital symmetry in **3** than in **1** or **2**.

In order to find a transition state for the closure of **3** to **7**, the C-1 - C-3 distance in **3** was iteratively shortened from the distance of 2.39Å in the diradical to the optimized bond length of 1.53Å in **7**; and at each point the geometry was optimized with this distance fixed. Starting from the structure of highest energy that was found by this scan, the actual transition state was located. Vibrational analysis confirmed that it was a transition state, and following of the intrinsic reaction coordinate showed it to be the transition state for the closure of **3** to **7**.

The geometry of the transition state is shown in Figure 4.2. It has only C_1 symmetry; so the pathway from **3** to it cannot be purely disrotatory. Indeed, since the equilibrium geometry of **3** has C_2, rather than C_s symmetry, the reaction path for disrotatory ring closure must in its early stages have only C_1 symmetry. Since, as expected from Hammond's postulate, the transition state resembles the geometry of **3** more than **7**, it is perhaps not surprising that it deviates significantly from C_s symmetry.

The energy barrier for ring closure of **3** to **7** is predicted to be 9.5 kcal/mol at the TCSCF level of theory and 14.5 kcal/mol at the CASPT2 level. After correction for differences in zero-point energies and heat capacities, the latter value yields $\Delta H^{\ddagger}_{298}$ = 13.5 kcal/mol. This large barrier should prevent **3** from closing to **7** at moderately low temperatures. Unfortunately, **3** probably has a low barrier for rearrangement via a [1,2] sigmatropic silyl shift,[19] which will prevent **3** from having significant kinetic stability.

The energy difference between **3** and **7** is only 24.5 kcal/mol at the CASPT2 level. Since vinyl groups at C-1 and C-3 might provide about this amount of allylic stabilization for the diradical,[12] we undertook calculations to test computationally whether vinyl substituents at these two carbons would actually make the 1,3-divinyl derivative, **4**, stable toward ring closure to **8**.

The lowest singlet and triplet states of diradical **4** were optimized with C_{2v} and C_2 symmetries. As with **3**, the C_2 structures were found to be the lower in energy. The singlet-triplet gap in **4** is -0.8 kcal/mol at the (6/6)CASSCF level and -2.1 kcal/mol at CASPT2.

The much smaller magnitude of the singlet-triplet gap in **4** than in **3** is obviously due to conjugation of the radical centers with the vinyl groups in **4**. Allylic delocalization reduces the magnitude of the coefficients of the in-phase combination of p-π orbitals at C-1 and C-3 and thus decreases the destabilization of the nonbonding MO that results from interaction of this combination with the C-Si bonds. The resulting reduction in the energy difference between this nonbonding MO and the nonbonding MO that involves the out-of-phase combination of p-π orbitals at C-1 and C-3 selectively stabilizes the triplet relative to the singlet.

As shown in Table 4.1, the energy difference between **4** and **8** is nearly zero at the (6/6)CASSCF level. Unfortunately, performing CASPT2 calculations on **8** in

C_1 symmetry required disk storage in excess of that available to us. However, we were able to perform CASPT2 calculations on **8** in C_s symmetry. Since our calculations found that the CASPT2 energy difference of 0.16 kcal/mol between the C_s and C_1 geometries of **7** is almost exactly the same as the TCSCF energy difference, we assume that the CASPT2 and (6/6)CASSCF energy differences between these two geometries of **8** are also the same. Adding this energy difference of 0.4 kcal/mol between the C_s and C_1 geometries of **8** to the CASPT2 energy difference of 0.4 kcal/mol between **4** and the C_s geometry of **8** gives an estimate of 0.8 kcal/mol for the difference between the CASPT2 energies of the equilibrium geometries of **4** and **8**.

CASPT2 is known to overestimate the resonance stabilization energy of allyl radical by 1 - 2 kcal/mol;[12] so our CASPT2 calculations suggest that, although the C-1 - C-4 bond in **8** is weak, it does have a positive dissociation energy. Since phenyl substituents would each be expected to provide 1 - 2 kcal/mol less resonance stabilization than the vinyl substituents provide for **4**,[12] it seems highly likely that the C-1 -C-4 bond in the 1,4-diphenyl derivative of **7** also has a positive BDE.

Even though **4** is not predicted to be thermodynamically stable with respect to closure to **8**, ring closure of **4**, like that of **3**, should encounter a sizable kinetic barrier. Unfortunately, the C_1 geometry of the transition state for ring closure of **4** prevented us from performing CASPT2 calculations on it. However, the CASSCF energy of the C_s constrained transition state is only 0.03 kcal/mol higher than that of the C_1 transition state; so we expect their CASPT2 energies also to be essentially the same. Therefore, 12.8 kcal/mol should provide a very good estimate of the CASPT2 energy difference between **4** and the C_1 transition state for its closure to **8**.

Conclusions

The high barriers to ring closure predicted for diradical **4** and, by inference,[12] its diphenyl analog make these derivatives of **3** potentially kinetically stable singlet diradicals. Additionally, the allylic and benzylic chromophores that are present in these derivatives should facilitate the detection of these diradicals and allow the rates of ring closure and reaction to be conveniently monitored by UV spectroscopy.[8]

On the other hand, the singlet-triplet splitting of only -2.1 kcal/mol that is predicted for **4** at the CASPT2 level is uncomfortably small. Since in benzylic radicals the unpaired electrons are slightly more localized than in allylic radicals,[12] the 1,3-diphenyl derivative of diradical **3** would be expected to have a singlet-triplet energy splitting that is larger than that in the divinyl derivative (**4**), although certainly not as large as the CASPT2 value of -5.8 kcal/mol in **3** itself.

The angle constraints that are present in the five-membered ring of **3** are computed to make the singlet-triplet splitting in this diradical considerably smaller than in the acyclic 2,2-disilyltrimethylene diradical. Nevertheless, the singlet is predicted to be the ground state by a sufficiently large margin in **3** that this diradical and hopefully also its 1,3 diphenyl analog could be used to test the prediction[9] that silyl groups at C-2 of 1,3-diradicals should confer upon them singlet ground states. However, the computed barriers for silyl migrations in some 2,2-disilyl-1,3-diradicals are rather low;[19] so **3** and **4** may rearrange too quickly to allow confirmation of the prediction that they have singlet ground states.

Table 4.1. Calculated TCSCF,[a] ROHF,[b] (6/6)CASSCF,[c] CASPT2/6-31G*, and Zero-Point Relative Energies (kcal/mol) for the Stationary Points on the Singlet and Triplet Potential Surfaces for 2,2-Disilylcyclopentane-1,3-diyl (**3**) and for 2,2-Disilyl-1,3-divinylcyclopentane-1,3-diyl (**4**)

Species	symmetry	SCF	PT2	ZPE
3 (^{1}A)	C_2	0[d]	0[e]	0[f]
3 ($^1A_1$)	C_{2v}	2.2	1.1	-2.0
3 (^{1}A')	C_s	2.1	1.7	-1.3
3 (^{3}B)	C_2	2.9	5.8	-0.7
3 ($^3B_2$)	C_{2v}	3.9	5.8	-2.1
3 (^{3}A")	C_s	3.6	6.5	-1.1
7 (^{1}A)	C_1	-20.8	-24.5	2.2
TS (**3** --> **7**)	C_1	9.5	14.5	-0.6
4 (^{1}A)	C_2	0[g]	0[h]	0[i,j]
4 (^{3}B)	C_2	0.8	2.1	---
8 (^{1}A)	C_1	-0.1	-0.8[j]	-0.16[j]
TS (**4** --> **8**)[k]	C_1	14.4	12.8[j]	-2.27[j]

[a] For singlets **3**, **7**, and the transition state for closure of **3** to **7**. [b] For triplet **3**. [c] For singlet and triplet **4**, **8**, and the transition state for closure of **4** to **8**. [d] *E*(TCSCF/6-31G*) = -774.062267 hartrees. [e] *E*(CASPT2/6-31G*) = -774.898575 hartrees. [f] ZPE = 96.5 kcal/mol. [g] *E*((6/6)CASSCF/6-31G*) = -927.910468 hartrees. [h] *E*(CASPT2/6-31G*) = -929.233530 hartrees. [i] ZPE = 139.66 kcal/mol. [j] Although every gradient in these vibrational analyses was close to zero, some of the displacements, corresponding to rotation of the *endo* silyl group, were larger than the default limits for convergence. [k] CASPT2 energy estimated from the CASPT2 energy in C_s symmetry and the (6,6)CASSCF energy difference between these two geometries.

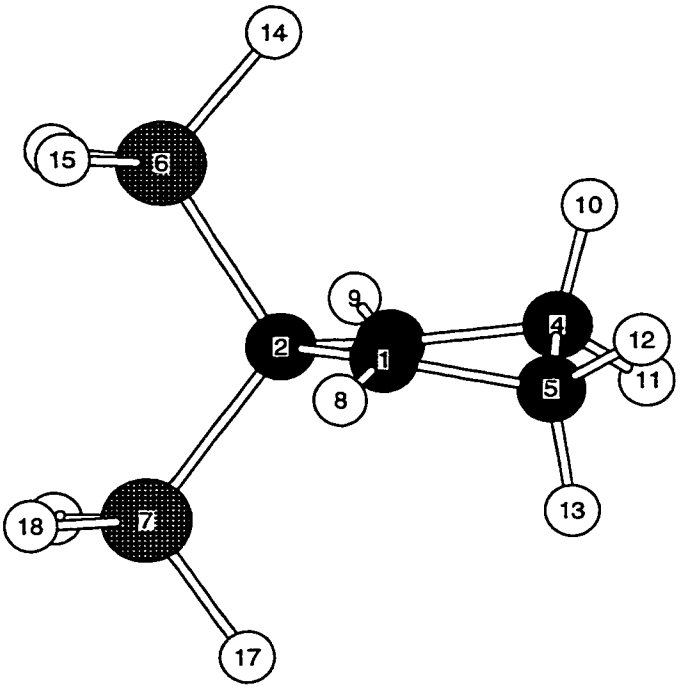


Figure 4.1: The optimized C_2 geometry for ^{1}A 2,2-disilylcyclopentane-1,3-diyl (**3**).

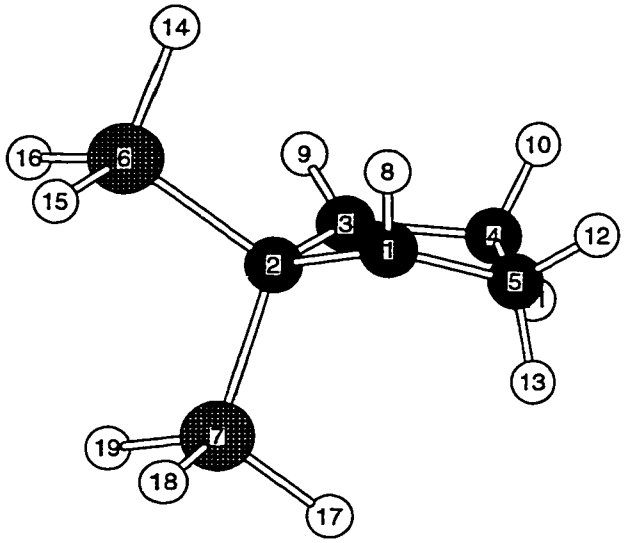


Figure 4.2: The C_1 transition state for the ring closure of 2,2-disilylcyclopentane-1,3-diyl (**3**) to 5,5-disilylbicyclo[2.1.0]pentane (**7**).

Chapter 4 Notes

1. (a) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857. (b) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

2. Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1979**, *101* 2245.

3. Sherrill, C. D.; Seidl, E. T.; Schaefer, H. F. *J. Phys. Chem.* **1992**, *96*, 3712.

4. Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* , **1988**, *110*, 2681.

5. (a) Doubleday, C.; McIver, J. W.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533. (b) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.

6. (a) Getty, S. J.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1521. (b) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689.

7. Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 5425.

8. Adam, W.; Borden, W. T.; Burda, C.; Foster, H.; Heidenfelder, T.; Heubes, M.; Hrovat, D. A.; Kita, F.; Lewis, S. B.; Scheutzow, D.; Wirz, J. *J. Am. Chem. Soc.* **1998**, *120*, 593.

9. Skancke, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 7079.

10. Baldwin, J. E.; Ollerenshaw, J. *J. Org. Chem.*, **1981**, *46*, 2116.

11. (a) Coms, F. D.; Dougherty, D. A., *J. Am. Chem. Soc.*, **1989**, *111*, 6894. (b) Adam, W.; Platsch, H. *J. Am. Chem. Soc.* **1989**, *111*, 6896.

12. Hrovat, D. A.; Borden, W. T. *J. Phys. Chem.* **1994**, *98*, 10460, and references cited therein.

13. Ellison, G. B.; Davico, G. E.; Bierbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrom., Ion Proc.* **1996**, *156*, 109.

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

15. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1995.

16. Review: Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

17. Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

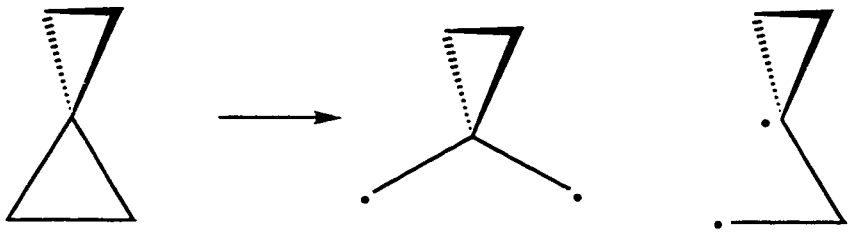
18. Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O., MOLCAS-3, University of Lund, Sweden

19. The barrier for a [1,2] silyl shift in some 3,3-disilylpentane-2,4-diyls have been calculated to be very low. Hrovat, D. A.; Borden, W. T. Unpublished results.

Chapter 5:

Ab Initio Calculations on Spiropentane Stereomutations Lead to a Reinterpretation of the Experimental Results

The first study of the stereomutation of spiropentane (**1**) was published thirty years ago.[1] Gilbert reported that, upon heating, *cis*-1,2-$^2H_2$-spiropentane isomerizes to *trans*-1,2-$^2H_2$-spiropentane, prior to undergoing structural rearrangement.[2] Subsequently, Gajewski and Burka pyrolyzed the proximal, medial, and distal stereoisomers of 1,4-dimethylspiropentanes;[3] and from the kinetics of interconversion that they observed, they concluded that fission of a peripheral bond, to form diradical **2**, is preferred to cleavage of a radial bond, to form diradical **3**. Stereomutation of **1** by exclusive formation of 1,1-dimethylenecyclopropane (**2**), is supported by the results of additional experiments by Gajewski.[4]



1 **2** **3**

Gajewski and Chang (G&C) investigated the pyrolyses of *syn*-4,4-$^2H_2$-*cis*-1,2-dimethylspiropentane (**4**-$^2H_2$, see Figure 5.1) and of optically active *trans*-1,2-dimethylspiropentane (**7**) at 290°.[5a] Coupled rotation was found to be slightly favored over monorotation in both spiropentanes. G&C based their assignment of the mode of coupled rotation that is preferred on the experimental finding that double rotation is favored over monorotation by a factor of 3.6 in the pyrolysis of **4**-$^2H_2$ and by a factor of only 1.4 in the pyrolysis of **7**.

Based on the experimental results in the pyrolyses of other hydrocarbons, G&C assumed that "outward" rotation of a methyl group in **4** and **7** is sterically less demanding than "inward" rotation. Therefore, they expected formation of diradical **5** to provide a lower energy pathway for double rotation than formation of diradical **6**. This assumption, together with the modes of coupled rotation that connect **4** and **7** to **5** and **6** (shown in Figure 5.1), resulted in G&C's interpreting the experimental ratios of single to double rotation in **4** and **7** as indicating that disrotation is preferred to conrotation in the stereomutations of these spiropentanes.

The apparent preference for disrotation, rather than conrotation, in the pyrolyses of **4** and **7** was unexpected. In 1968 Hoffmann published the results of Extended Hückel (EH) calculations on the ring opening of cyclopropane, which predicted a large preference for conrotation over both dis- and monorotation.[6] Hoffmann showed that this preference arises from hyperconjugative electron donation from the C-H bonds at C-2 into the in-phase (b_1) combination of p-π AOs at the terminal carbons in the (0,0) conformation of the trimethylene diradical (shown in Figure 5.2). Although subsequent *ab initio* calculations have found a much smaller preference than the EH calculations for conrotation [via the (0,0) geometry] over both disrotation and monorotation [via a (0,90) geometry], the qualitative preference for conrotation does persist at the highest levels of theory.[7]

At least in the stabilization of carbocations, the strained C-C bonds of cyclopropane rings are known to be better hyperconjugative electron donors than C-H bonds.[8] Therefore, if a preference for coupled rotation were observed in the stereomutation reactions of derivatives of **1**, such as **4** and **7**, one would have expected that the preferred mode of coupling would have been found to be conrotatory.[9] Thus, if correct, the conclusion that disrotation is preferred in the stereomutation reactions of **4** and **7** is surprising, especially in light of more recent

calculations which show that disrotation is expected only when the bonds at C-2 that hyperconjugate with the p-π AOs at C-1 and C-3 are electron *acceptors*, *not donors.*[10] The strong preference for disrotation, predicted in the stereomutation of 1,1-difluorocyclopropanes, has, in fact, been experimentally confirmed.[11]

Nevertheless, when G&C reinvestigated the thermal isomerizations of the four 1,2,4-trimethylspiropentanes,[5b] using optically active *trans* compounds,[5a] they again found that, as in **4** and **7**, the ratio of double to single rotation is about a factor of three larger in each of the two *cis* stereoisomers than in each of the two *trans* compounds. This result was interpreted as additional evidence for the conclusion, drawn from the study of dimethylspiropentanes **4** and **7**, that disrotation is preferred to conrotation in spiropentane stereomutation reactions.

The trimethylspiropentane experiments also led to another unexpected observation. In each of the two *trans* compounds epimerization of the C-4 methyl group (by some combination of single rotation of C-4 and double rotation of C-4 in concert with C-5, the unsubstituted carbon) is roughly a factor of five faster than double rotation of C-1 and C-2. This result is surprising because epimerization at C-4 proceeds through a diradical that has one primary center (C-5), while coupled rotation of C-1 and C-2 produces a diradical with two secondary centers.

In order to try to understand why disrotation is apparently preferred to conrotation in the pyrolyses of both the 1,2-dimethyl- and the 1,2,4-trimethylspiropentanes, I carried out *ab initio* calculations of the potential surfaces for the stereomutations of **1**, **4**, and **7**. We have also investigated why double rotation of C-1 and C-2 in the *trans*-1,2,4-trimethylspiropentanes is slower than epimerization at C-4. Herein we report the results of our calculations, which lead to a reinterpretation of the experimental results of G&C.[5a]

Methodology

All calculations were performed with the 6-31G* basis set.[12] Geometries of alkanes were optimized at the RHF level of theory, and geometries of monoradicals and triplet diradicals were optimized at the ROHF level. Singlet diradical geometries were optimized with (2/2)CASSCF wavefunctions. The geometries of stationary points were located and vibrational analyses were performed with Gaussian 94.[13]

The effects of including dynamic electron correlation[14] were investigated by performing CASPT2 calculations,[15] for which the RHF, ROHF and (2/2)CASSCF wave functions were used as the references. A CASPT2 calculation with an RHF wave function as the reference is an MP2 calculation, and our MP2 calculations were carried out with Gaussian 94.[13] All the other CASPT2 calculations and ROMP2 calculations on some monoradicals were performed with the MOLCAS suite of *ab initio* programs.[16]

Results and Discussion

Stereomutation of Spiropentane (1) The geometry of 1 was optimized in D_{2d} symmetry and was shown to be a minimum by a vibrational analysis. The (0,0) geometry of 1,1-dimethylenecyclopropane (2) was optimized in C_{2v} symmetry, but 2-(0,0) was found to have three modes with imaginary frequencies. These modes involved *syn* and *anti* pyramidalization of the two radical centers and conrotation of both methylene groups.

Other stationary points located on the potential surface for the stereomutation of **1** were a C_2 transition state for conrotation in diradical **2** (**2-con**), a C_s transition state for disrotation in **2** (**2-dis**), and a diradical energy minimum (**2-min**), also with C_s symmetry. The last of these stationary points connects two conrotatory transition

states. The lowest frequency vibration in **2-min** is computed to be only 5 cm^{-1}; so **2-min** exists in a very shallow energy well.[17]

As shown in Table 5.1, the (2/2)CASSCF energies of **2-con** and **2-(0,0)** are identical to within 0.1 kcal/mol. This is not too surprising since the geometry of **2-con** differs from that of **2-(0,0)** by a mere 9.1° of conrotation. As usual, upon including dynamic electron correlation, the more delocalized structure is selectively stabilized,[14] and the CASPT2 energy of **2-(0,0)** is found to be slightly lower than those of both **2-con** and **2-min**. On the CASPT2 potential energy surface **2-(0,0)**, or a geometry very close to it, is probably the transition state for conrotatory opening and closure of **1**.

The geometry of the (0,90) conformer of **2** was optimized in C_s symmetry, but **2-(0,90)** was found to have two vibrational modes with imaginary frequencies, corresponding to pyramidalization and rotation of the methylene group that lies in the symmetry plane. Allowing this radical center to pyramidalize led to the monorotatory transition state (**2-mono**).

Using an optimized geometry for the radially-cleaved triplet diradical as a starting point, searching for a singlet transition structure led to the (2/2)CASSCF geometry of **3**. The relative (2/2)CASSCF and CASPT2 energies of **2-(0,90)**, **2-mono**, and **3** are given in Table 5.1.

After corrections for the ZPE and heat capacity differences, given in Table 5.1, the enthalpy of activation that we calculate at the CASPT2 level of theory for isomerization of **1** via rate-determining passage through **2-mono** is $\Delta H^{\ddagger}_{298}$ = 51.3 kcal/mol. This calculated value is in superb agreement with Gilbert's experimental value of $\Delta H^{\ddagger}_{298}$ = 50.9±1.0 kcal/mol for isomerization of *cis*-1,2-$^{2}H_2$-spiropentane to *trans*-1,2 -$^{2}H_2$-spiropentane. The (2/2)CASSCF value for $\Delta H^{\ddagger}$ is far too low, due to

the absence from these calculations of correlation for the electrons in all three of the strained σ bonds of the three-membered ring that undergoes opening.[7]

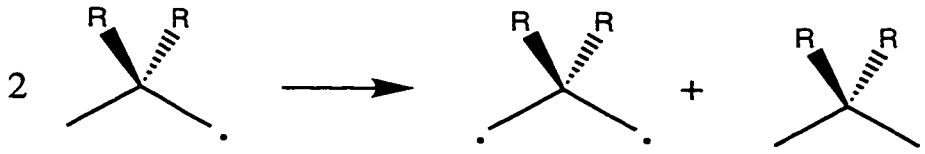
Also in agreement with experiment,[3,4] our calculations show that breaking a peripheral bond in **1** to form diradical **2** requires substantially less energy than cleaving a radial bond to form diradical **3**. The former diradical possesses one more bond to a cyclopropyl ring carbon than the latter, and the large amount of 2s character in this bond makes it stronger than the bond to the sp^3 carbon that is absent in **2** but present in **3**.[18,19]

Whether the energies of **2-con** and **2-mono** or **2-(0,0)** and **2-(0,90)** are compared, conrotation is computed to be preferred over monorotation in the stereomutation of **1** by 2.8 kcal/mol at the CASPT2 level of theory. The CASPT2 energy of the transition state for conrotation is lower than that for disrotation by about the same amount. These preferences for conrotatory ring opening of **1** are a little more than 1 kcal/mol larger than those computed for stereomutation of cyclopropane,[20] but they are much smaller than those calculated at the same level of theory for stereomutation of 1,1-disilylcyclopropane.[9b,21]

Hyperconjugation in 2-(0,0) At least some of the energetic preference for the (0,0) over the (0,90) conformation in diradical **2** has the same origin as the preference for the bisected (0) over the staggered (90) CH_2 conformation in cyclopropylcarbinyl monoradical. The bisected conformation allows the singly occupied π AO on the CH_2 group to be stabilized by interacting with both the bonding and antibonding Walsh orbitals of the cyclopropane ring that also have a" symmetry. The preference for the (0) over the (90) CH_2 conformation in cyclopropylcarbinyl radical is calculated to amount to 2.2 kcal/mol at the CASPT2 level of theory,[18] a value which is in very good agreement with the experimental value of 2.4 ± 0.5 kcal/mol.[22]

In contrast, the (0) and (90) conformations of the 1-propyl radical have the same energies to within 0.2 kcal/mol.[10b] The energy difference between the (0) and (90) CH_2 conformations in cyclopropylcarbinyl radical is thus ca. 2 kcal/mol larger than in propyl radical, and this might have been expected to be the amount by which the energy difference between the (0,0) and (0,90) conformations is larger in diradical **2** than in trimethylene. However, as already noted, the CASPT2 energy difference between the (0,0) and (0,90) conformations in **2** is only about 1 kcal/mol larger than in trimethylene.[20]

The somewhat smaller than expected energetic preference for (0,0) over (0,90) in **2** could be due to the hyperconjugative interaction of the two radical centers with the cyclopropane ring bonds in **2-(0,0)** being competitive, rather than cooperative. Whether the hyperconjugative interaction of radical centers at C-1 and C-3 with the exocyclic bonds to C-2 is competitive or cooperative in a 1,3-diradical can be assessed by computing the energy of the isodesmic reaction in equation 1.[10b] If the reaction is calculated to be energetically favorable, the interaction is



(1)

cooperative; but, if the reaction is calculated to be energetically unfavorable, the interaction is competitive. Strongly electron accepting bonds (e.g., R = F) or strongly electron donating bonds (e.g., R = SiR_3) at C-2 result in a cooperative interaction of the two radical centers. For example, for R = F the CASPT2 energy of the reaction in equation 1 is -3.8 kcal/mol,[10b] and for R = SiH_3 the reaction in equation 1 is computed to be energetically favorable by -10.1 kcal/mol at this level of theory.[9b] In contrast, for R = H, the reaction in equation 1 is computed to be unfavorable by 0.7

kcal/mol at the CASPT2 level, showing that the radical centers in (0,0)-trimethylene act competitively, rather than cooperatively.[9b,10b]

For R-R = H_2C-CH_2 the reaction in equation 1 is also computed to energetically unfavorable and actually by 0.4 kcal/mol more than in trimethylene. This result indicates that the cyclopropane ring in **2-(0,0)** is certainly not a significantly better hyperconjugative, two-electron donor than the C-H bonds at C-2 in (0,0)-trimethylene. This finding is quite surprising, since, as already noted, the strained C-C bonds of cyclopropane rings are known[8] to be much better hyperconjugative, two-electron donors than C-H bonds in the stabilization of carbocations.[23]

Another indication of whether the C-R bonds at C-2 in a 1,3-diradical either accept electron pairs from or donate electron pairs to the two radical centers is the singlet-triplet energy separation. Both the electron-accepting C-F bonds in (0,0)-2,2-difluorotrimethylene and the electron-donating C-Si bonds in (0,0)-2,2-disilyltrimethylene strongly lift the near degeneracy of the b_1 and a_2 NBMOs in these diradicals and result in each diradical being computed to have a singlet ground state.[9b,10b] At the CASPT2 level of theory, ΔE_{ST} = - 4.8 in the former[10b,24] and ΔE_{ST} = - 11.9 kcal/mol in the latter.[9b]

In the (0,0) conformation of the parent trimethylene diradical the interaction of the p-π AOs at C-1 and C-3 with the weakly electron-donating C-H bonds at C-2 is not very effective in lifting the degeneracy between the b_1 and a_2 combinations of these AOs. For R = H the orbital energy difference between b_1 and a_2 of 4.1 kcal/mol is only 20% as large as the value of 18.9 kcal/mol for R = SiH_3; and the occupation numbers of the b_1 and a_2 NBMOs in the (2/2)CASSCF singlet wavefunction for R = H are, respectively, 0.91 and 1.09, compared to 0.49 and

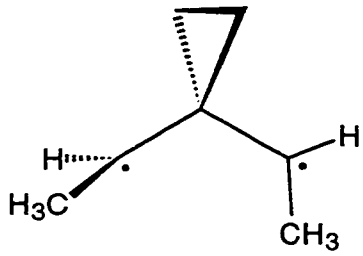
1.51 for R = SiH_3. Consequently, a triplet ground state with ΔE_{ST} = 0.7 kcal/mol is computed for (0,0)-trimethylene.[10b]

In **2-(0,0)** the b_1 orbital of the cyclopropane ring is slightly more effective than the b_1 combination of C-H bonds is in (0,0)-trimethylene at lifting the degeneracy of the b_1 and a_2 NBMOs. The ROHF orbital energies in **2-(0,0)** differ by 5.7 kcal/mol, 40% more than in (0,0)-trimethylene; and the occupation numbers of the a_2 and b_1 NBMOs in **2-(0,0)** are, respectively, 1.12 and 0.88, compared to 0.91 and 1.09 in (0,0)-trimethylene. Nevertheless, not only is **2-(0,0)** predicted to have a triplet ground state, but the CASPT2 value of ΔE_{ST} = 2.0 kcal/mol in **2-(0,0)** is nearly three times larger than ΔE_{ST} in (0,0)-trimethylene.[10b]

The value of ΔE_{ST} in a diradical depends not only on the energy difference between the NBMOs but also on the degree to which the GVB orbitals derived from them are disjoint.[25] The b_1 combination of p-π AOs at C-1 and C-3 interact more strongly with *both* the bonding and the antibonding b_1 cyclopropane Walsh orbitals in **2-(0,0)** than with the bonding and antibonding C-H orbitals in (0,0)-trimethylene. The larger amount of orbital mixing that results from this *pair* of interactions in **2-(0,0)** leads to its GVB orbitals being less disjoint than those in (0,0)-trimethylene.[26]

Stereomutation of 1,2-Dimethylspiropentanes (4 and 7) We have previously found that at the (2/2)CASSCF level of theory, terminal methyl groups reduce the energy difference of 0.7 kcal/mol between the (0,90) and (0,0) conformations of trimethylene to a difference of only 0.2 kcal/mol between (0,90) and the lowest energy *s-trans,s-trans*-(0,0) conformation of pentane-2,4-diyl.[10b] A similar effect is seen on comparison of the (2/2)CASSCF energies in Tables 5.1 and 5.2. At this level of theory the *s-cis* (**8**) and *s-trans* (**9**) monorotatory transition states for interconversion of *cis*- and *trans*-1,2-dimethylspiropentane (**4** and **7**) are

actually lower in energy than any of the other stationary points that we located on the potential surface for stereomutation of **4** and **7**. Presumably, hyperconjugation of the terminal methyl groups with the radical centers in diradicals **5**, **6**, **8**, and **9** reduces the importance of hyperconjugation of these centers with the strained C-C bonds of the cyclopropane ring.



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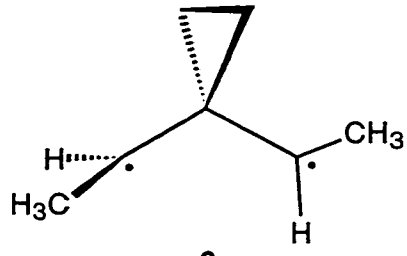

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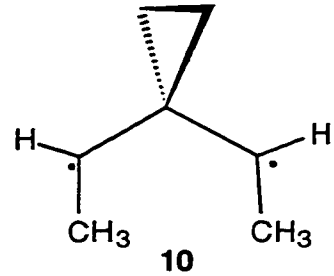


10

However, in addition to this electronic effect, Table 5.2 shows there are apparently also some steric effects on the relative energies of these diradical conformers, due to the presence of the cyclopropane ring. These effects make the *s-cis* methyl conformation relatively more favorable in **6** and **8** than in pentane-2,4-diyl. In the latter diradical the *s-trans,s-trans*-(0,0) conformation is favored over *s-cis,s-trans*-(0,0) by 1.2 kcal/mol at the (2/2)CASSCF level of theory.[10b] In contrast, **8** is calculated to be within 0.2 kcal/mol of **9** at both the (2/2)CASSCF and CASPT2 levels of theory; and **6** is actually calculated to be lower in energy than **5** by 0.8 kcal/mol at (2/2)CASSCF and by 1.6 kcal/mol at CASPT2. With inclusion of dynamic electron correlation at the latter level of theory, **6** becomes the lowest energy diradical stationary point that we located.[27]

The rather surprising finding that the *s-cis,s-trans* conformation of diradical **6** is lower in energy than the *s-trans,s-trans* conformation of diradical **5** prompted us also to compute the energy of the *s-cis,s-cis* conformation of diradical **10**. In the latter conformation there is considerable steric crowding between the two "inward-rotated"

methyl groups. Consequently, as shown in Table 5.2, **10** is computed to be higher in energy than either **5** or **6** at both the (2/2)CASSCF and CASPT2 levels of theory.

Our finding that *s-cis,s-trans*-(0,0) diradical conformation (**6**) is lower in energy than the *s-trans,s-trans*-(0,0) conformation (**5**) has profound implications for interpreting the experiments of G&C.[5a] As discussed above, these experiments found that the ratio of double to single rotation is higher in **4** than in **7**; and G&C correctly interpreted this finding as being due to **4** undergoing ring opening to the more stable (0,0) diradical conformation. However, G&C made the reasonable but incorrect assumption that diradical **5** is lower in energy than **6**. Since, as shown in Figure 5.1, **4** must open to **5** by disrotation, G&C concluded that disrotation is preferred to conrotation in the stereomutations of **4** and **7**.

Not only do our calculations find, in contrast to what G&C assumed, that **6** is lower in energy than **5**; but, in addition, the *s-cis,s-trans* conformation of **6** is favored by a statistical factor of two over the *s-trans,s-trans* conformation of **5**. Therefore, we reinterpret the results of G&C's experiments as having shown that the ratio of double to single rotation is higher in **4** than in **7**, because **4** preferentially undergoes ring opening *not* to **5** but to **6**.[28] Since, as illustrated in Figure 5.1, **4** opens to **6** by conrotation, we conclude that conrotation is preferred to disrotation in the stereomutations of **4** and **7**.

This conclusion is in accord with the expectation, based on qualitative theory and discussed above, that since the cyclopropane ring in **5** and **6** is a hyperconjugative electron donor, conrotatory ring opening of these spiropentanes should be preferred. Our reinterpretation of the experimental results of G&C is also consistent with the results of our calculations on the stereomutation reactions of **1**, **4**, and **7**. As shown in Tables 5.1 and 5.2, we find that at the CASPT2//(2/2)CASSCF

level of theory the disrotatory transition states are 2 - 3 kcal/mol higher in energy than their conrotatory counterparts.

In agreement with the experimental results of G&C is our finding that at the CASPT2//(2/2)CASSCF level of theory transition states **8** and **9** for effecting the interconversion of **4** and **7** by monorotation are both higher in energy than the preferred transition states for ring opening of **4** and **7** by double rotation.[29] In addition, and also as found experimentally by G&C, our calculations predict that the ratio of double to single rotation should be larger in **4** than in **7**.

As shown in Table 5.2, at both the CASSCF and CASPT2 levels **6-con**, the preferred transition structure for double rotation in the ring opening of **4**, is computed to be slightly lower in energy than **5-con**, the preferred transition structure for double rotation in the ring opening of **7**.[28] Since monorotation transition structures **8** and **9** are each accessible from both **4** and **7**, the 0.3 kcal/mol lower enthalpy of **6-con**, relative to **5-con**, predicts that at 560 K the ratio of conrotation to monorotation should be a factor of just 1.3 larger in **4** than in **7**. However, **6-con** is also statistically favored over **5-con** by a factor of two, so that our calculations predict that the ratio of conrotation to monorotation at 560 K should actually be a factor of 2.6 larger in **4** than in **7**. Probably fortuitously, this is *exactly* the factor by which the experiments of G&C[5a] found the ratio of double to single rotations to be larger in the stereomutation of **4** than of **7**.[29]

1,2,4-Trimethylspiropentanes As discussed in the introduction, the experiments of G&C also found that epimerization of C-4 in 11 and 13 (see Figure 5.3), the two *trans* stereoisomers of 1,2,4-trimethylspiropentane, is about five times faster than the rate of double rotation of C-1 and C-2. Presumably, this unexpected finding, that the less substituted peripheral bond preferentially cleaves, is due to both 11 and 13 undergoing conrotatory ring opening to an *s-trans,s-trans*-(0,0)

diradical geometry upon cleavage of the more substituted peripheral bond. In contrast, cleavage of the less substituted peripheral bond allows the C-4 methyl to epimerize via an *s-cis*-(0,0) geometry (12a). Based on the relative CASPT2 energies of 5 and 6 in Table 5.2, an *s-cis* methyl group should be preferred to an *s-trans* methyl group by 1.6 kcal/mol; and the two *s-trans* methyl groups in diradical 14 might prove sufficient to favor conrotation of C-4 and C-5 over conrotation of C-1 and C-2 in the ring opening of 11.

In order to test whether this is indeed the case, we carried out calculations on *s-cis* (**12a**) and *s-trans* (**12b**), the two (0,0) conformations of the diradical formed by cleavage of the bond between C-4 and C-5 in 1,2,4-trimethylspiropentane, **11**, and on **14**, the (0,0)-*s-trans*,*s-trans* conformation of the diradical formed by conrotatory cleavage of the bond between C-1 and C-2 in **11**. Diradicals **12a** and **12b** are the two idealized transition structures for interconversion of **11** and **13** by double rotations; and diradical **14** is the idealized transition structure for the preferred mode of double rotation by which **11** isomerizes to the enantiomer of **13** (**13'**).

Our calculations find that **12a** is favored over **12b**, by 3.0 kcal/mol at the (2/2)CASSCF level and by 4.0 at CASPT2. These energy differences are larger than those between **6** and **5** at these two levels of theory, which, as shown in Table 5.2, amount to only 0.7 and 1.6 kcal/mol, respectively. The larger energy differences between **12a** and **12b** can be ascribed in part to the presence in these two diradicals of the *trans* methyl groups, one of which sterically destabilizes the *s-trans* methyl group in **12b** more than the *s-cis* methyl group in **12a**.

The same type of steric interaction is present in **14** too, and it also serves to destabilize **14**, relative to **12a**. The (2/2)CASSCF energy of **12a** is computed to be lower than that of **14** by 2.7 kcal/mol, and CASPT2 calculations find this energy difference to increase to 3.8 kcal/mol. The size of the calculated energy difference

between these two diradicals is large enough to account easily for the factor of 5 by which G&C found the rate of interconversion of **11** and **13** to be faster than the rate of interconversion of **11** and **13'** at 290°.

Why Is the *s-cis* Methyl in 6 Preferred to the *s-trans* Methyl in 5? Previous studies have provided evidence for a long-range electronic interaction between an *s-cis* methyl at C-1 and the non-bonding p-π AO at C-3 in 1,3-diradicals.[10b] With hyperconjugatively electron accepting C-F bonds at C-2, this interaction is computed to be destabilizing. This leads to a large preference for (0,0)-*s-trans,s-trans* over (0,0)-*s-cis,s-trans* transition structures being both predicted[10] and found[11] in the stereomutations of 1,1-difluoro-2,3-dialkyl-cyclopropanes.

However, with hyperconjugatively electron donating bonds at C-2, the long-range electronic interaction between an *s-cis* methyl at C-1 and the non-bonding p-π AO at C-3 is expected to be stabilizing.[10b] Thus, the weakly electron donating C-H bonds at C-3 in pentane-2,4-diyl result in the energy difference between the *s-cis,s-trans* and the *s-trans,s-trans*-(0,0) conformations being computed to be three times smaller in the hydrocarbon than in the fluorocarbon diradical.[10b]

As shown by the relative energies of **5** and **6** in Table 5.2, the (0,0)-*s-cis,s-trans* conformation of the former is actually lower in energy than the (0,0)-*s-trans,s-trans* conformation of the latter. This reversal in conformational preference from that calculated for the (0,0) diradicals formed by conrotatory opening of *cis*- and *trans*-1,2-dimethylcyclopropane could either be due to steric destabilization of an *s-trans* methyl group in **5**, or to electronic stabilization of the *s-cis* methyl group in **6**, or to a combination of both these effects.

In order to assess the relative contributions of electronic and steric effects to the energetic preference for **6** over **5**, we compared the size of the energy

difference between them to that between the *s-cis* (**15d**, see Figure 5.4) and *s-trans* (**16d**) conformations of a closely related monoradical. In both **15d** and **16d** a C-H bond at C-3 was constrained to eclipse the bond between C-1 and C-2, so that, the orientation of the "inward" hydrogen at C-3 in **15d** and **16d** was similar to that of the hydrogen at C-3 in **6** and **5**. We also compared the energy differences between the *s-cis* and *s-trans* methyl conformations of the analogous monoradicals and diradicals with geminal hydrogens, fluorines, and silyl substituents at C-2. The results of these calculations are given in Table 5.3.

The differences in energy between the *s-cis* (**15**) and *s-trans* (**16**) conformations of the monoradicals should largely reflect the differences in the diradicals between the steric interactions of the *s-cis* methyl at C-1 in **6** and **17** with the in-plane hydrogen at C-3 and of the *s-trans* methyl in **5** and **18** with the geminal substituents, R, at C-2. The results in Table 5.3 for the monoradicals show that the *s-trans* methyl conformation in **16** is favored over the *s-cis* conformation in **15** by about the same amount for R = H and R = F. For R-R = H_2C-CH_2, the more sterically demanding ethano group at C-2 makes conformation **15d** only slightly higher in energy than **16d**. The larger still geminal silyl groups in **15c** and **16c** lead to the *s-cis* methyl conformation of the former actually being favored. The energy differences between conformations **15** and **16** are nearly the same at both the ROHF and ROMP2 levels, as might be expected for energy differences that are largely steric in origin.

In diradicals **6** and **17** only for R = F is the preference for an *s-trans* methyl conformation enhanced, relative to that in the corresponding monoradical. As already noted, with hyperconjugatively electron accepting C-F bonds at C-2, the long-range interaction between the *s-cis* methyl at C-1 and the non-bonding p-π AO at C-3 is destabilizing.[10b] This destabilizing electronic interaction in **17b** results in a 1.4 - 1.9

kcal/mol greater energetic preference for the *s-trans* conformation in diradical **18b** than in monoradical **16b**.

For electron donating C-R bonds at C-2 in the 1,3-diradicals the long-range interaction between the *s-cis* methyl at C-1 and the non-bonding p-π AO at C-3 is stabilizing.[10b] As already discussed in the comparison of diradical **2** with trimethylene, C-H bonds and cyclopropane C-C bonds at C-2 appear to have nearly comparable electron donating abilities in 1,3-diradicals; and both of these types of bonds at C-2 are significantly less good hyperconjugative electron donors than C-Si bonds. Therefore, it is not surprising that for R = H and for R-R = H_2C-CH_2, the preferences for the *s-cis* conformation in diradicals **17a** and **6** are only slightly greater than in monoradicals **15a** and **d**, respectively, amounting to ca. at 1 kcal/mol at the (CAS)SCF level and 2 kcal/mol at CASPT2. However, for R = SiH_3, the preference for an *s-cis* methyl conformation is much larger in diradical **17c** than in monoradical, amounting to 5.9 kcal/mol at the CASPT2 level.[30]

As shown in Table 5.3, the difference between the preferences for *s-cis* methyl conformations in the diradicals and in the monoradicals increases on going from (2/2)CASSCF/ROHF to CASPT2/ROMP2, and this increase is two to three times larger for R = SiH_3 than for R = H and R-R = H_2C-CH_2. Inclusion of dynamic electron correlation generally enhances electron delocalization;[14] and delocalization increases the attractive interaction between an *s-cis* methyl at C-1 and the non-bonding p-π AO at C-3 in the diradicals. The enhancement of this attraction by inclusion of dynamic electron correlation is greatest for geminal silyl groups at C-2, because hyperconjugative donation of electrons from the C-R bonds at this carbon to the in-phase combination of p-π AOs at C-1 and C-3 is much larger for R = SiH_3 than for R= H or R-R = H_2C-CH_2.

Conclusions

My calculations find that spiropentane (**1**) prefers conrotatory over monorotatory and disrotatory ring opening by only a slightly larger amount than cyclopropane. Moreover, at least part of this increased preference for conrotatory ring opening of **1** to the (0,0) conformation of diradical **2** resides in the preference for a bisected (0) conformation in cyclopropylcarbinyl monoradical. Despite the well known ability of cyclopropane C-C bonds to stabilize carbocations hyperconjugatively,[8] neither the energies calculated for the isodesmic reaction in equation 1 for R = H and for R-R = H_2C-CH_2 nor the sizes of ΔE_{ST} computed in **2** and in (0,0) trimethylene, indicate that the cyclopropane ring in the former diradical is a significantly better hyperconjugative electron donor than the C-H bonds in the latter.[23]

The weak electron donation from the cyclopropane ring in diradical **2** is further reduced by the presence of the methyl groups in diradicals **5** and **6**. Nevertheless, at the CASPT2 level of theory, conrotation is the preferred pathway for ring opening of *cis*-1,2-dimethylspiropentane (**4**) and of the *trans* isomer (**7**). The larger computed preference for double rotation over monorotatory ring opening in **4** than in **7** is in agreement with the experimental results of G&C.[5a]

However, in contrast to the assumption made by these authors, my calculations find that diradical **6** is lower in energy than diradical **5**; and, in addition, **6** is statistically favored over **5** by a factor of two.[29] Consequently, the reason double rotation is both computed and found to be preferred by more in the stereomutation of **4** than of **7** is not that **4** undergoes disrotatory opening to **5**, as concluded by G&C. Quite the opposite, the larger preference for double rotation found in **4** is due to the fact that the transition structure (**6-con**) for *conrotatory* opening of **4** to diradical

6 has a lower free energy than the transition structure (**5-con**) for *conrotatory* opening of **7** to diradical **5**.

Contributing to the lower electronic energy of the *s-cis* methyl conformation in **6**, relative to the *s-trans* methyl conformation in **5** is a weak long-range attraction between the *s-cis* methyl group and the non-bonding p-π AO at C-3. Our calculations find that the much more strongly electron donating C-Si bonds at C-2 in **17c** make the long-range attraction between the *s-cis* methyl and the p-π AO at C-3 much stronger in this diradical than in **6**; whereas, the electron accepting C-F bonds at C-2 in **17b** make the interaction between the *s-cis* methyl and p-π AO at C-3 repulsive in this diradical.

Table 5.1. Relative RHF, MP2, (2/2)CASSCF, and CASPT2, and Zero-Point Energies, Heat Capacity Corrections at 298 K, and Relative Enthalpies for the Stationary Points on the Singlet Potential Surfaces for Spiropentane, all in kcal/mol.

Species	Symmetry	SCF[a]	PT2[b]	ZPE	$C_{v,298}$ x 298°	DH_{298} (SCF)	DH_{298} (PT2)
1 ($^1A_1$)	D_{2d}	-35.9	-52.8	5.8	-1.3	-31.4	-48.3
2-con (^1A)	C_2	0.0[c]	0.0[d]	0.0[e]	0.0[f]	0.0	0.0
2-dis ($^1A'$)	C_s	0.7	3.0	0.3	-0.2	0.8	3.1
2-mono (^1A)	C_1	0.8	2.8	0.4	-0.2	1.0	3.0
3 (^1A)	C_1	6.6	10.7	1.5	-0.6	7.4	11.6
2-min ($^1A'$)	C_s	-0.4	0.4	0.7	0.3	0.6	1.4
2-(0,0) ($^1A_1$)	C_{2v}	0.1	-0.2	-0.8[g]	-1.0[g]	-1.7	-2.0
2-(0,90) ($^1A'$)	C_s	1.0	2.6	-0.2[h]	-0.6[h]	0.1	1.8

[a] RHF for **1**, (2/2)CASSCF for all diradicals. [b] MP2 for **1**, CASPT2 for all diradicals. [c] E((2/2)CASSCF) = -193.8606134 hartrees. [d] E(CASPT2) = -194.5045976 hartrees. [e] ZPE((2/2)CASSCF) = 71.86 kcal/mol. [f] $C_{v,\ 298}$ ((2/2)CASSCF) = 21.16 e.u. [g] The idealized geometry, **2-(0,0)** has three modes with imaginary frequencies. [h] The idealized geometry, **2-(0,90)** has two modes with imaginary frequencies.

Table 5.2. Relative RHF, MP2, (2/2)CASSSCF, CASPT2, and Zero-Point Energies, Relative Heat Capacitiy Corrections at 560K, and Relative Enthalpies of the Stationary Points on the Singlet Potential Surfaces for 1,2-Dimethylspiropentane, all in kcal/mol.

Species	Symmetry	SCF[a]	PT2[b]	ZPE	$C_{v,\,560}$ x 560°	DH_{560} (SCF)	DH_{560} (PT2)
4 (^{1}A')	C_s	-35.0	-51.7	3.6	-0.3	-31.7	-48.4
7 (^{1}A)	C_2	-36.4	-52.9	3.5	-0.3	-33.1	-49.6
6-con (^{1}A)	C_1	0.0[c]	0.0[d]	0.0[e]	0.0[f]	0.0	0.0
5-dis (^{1}A)	C_1	0.7	1.9	-0.2	0.1	0.5	1.7
8 (^{1}A)	C_1	-0.1	1.3	-0.4	0.1	-0.4	1.0
9 (^{1}A)	C_1	-0.3	1.5	-0.3	0.1	-0.5	1.2
5-con (^{1}A)	C_2	0.5	0.6	-0.5	0.2	0.2	0.3
6-dis (^{1}A)	C_1	0.4	2.5	-0.3	0.0	0.1	2.2
5-min (^{1}A')	C_s	0.5	1.0	-0.1	1.2	1.5	2.0
5 ($^1A_1$)	C_{2v}	1.6	0.9	-1.6[h]	-3.0[h]	-3.0	-3.7
6 (^{1}A')	C_s	0.9	-0.7	-1.4[g]	-1.9[g]	-2.4	-3.9
10 ($^1A_1$)	C_{2v}	3.9	2.4	-1.0[g]	-2.0[g]	0.9	-0.6

[a] RHF for **4**, and **7**, and (2/2)CASSCF for all diradicals. [b] MP2 for **4**, and **7**, and CASPT2 for all diradicals. [c] E(CASSCF) = -271.9341451 hartrees. [d] E(CASPT2) = -272.8540859 hartrees. [e] ZPE(2/2)CASSCF = 111.73 kcal/mol. [f] $C_{v,\,560}$ = 50.20 e.u. [g] **6** and **10** were shown to have three vibrational modes with imaginary frequencies. [h] **5** was shown to have four vibrational modes with imaginary frequencies.

Table 5.3. Relative ROHF, (2/2)CASSCF, and CASPT2 Energies for the *s-cis* -> *s-trans* Isomerization of Radicals **15** and **16** and of Diradicals **5**, **6**, **17**, and **18**.

Reaction	(CAS)SCF[a]	CASPT2[b]
18a -> 17a	1.2	0.3
16a -> 15a	2.2	2.0
18a + 15a -> 17a + 16a	-1.0	-1.8
18b -> 17b	3.5	4.1
16b -> 15b	2.1	2.2
18b + 15b -> 17b + 16b	1.4	1.9
18c -> 17c	-4.6[c]	-6.4[c]
16c -> 15c	-0.5[c]	-0.5[c]
18c + 15c -> 17c + 16c	-4.1[c]	-5.9[c]
5 -> 6	-0.7	-1.6
16d -> 15d	0.4	0.7
5 + 15d -> 6 + 16d	-1.1	-2.3

[a] ROHF for radicals and (2/2)CASSCF for diradicals. [b] ROMP2 for radicals and CASPT2 for diradicals. [c] For R = SiH_3 the lower energy conformation is the one in which a methyl C-H bond eclipses the C-C rather than the C-H bond at the radical center.

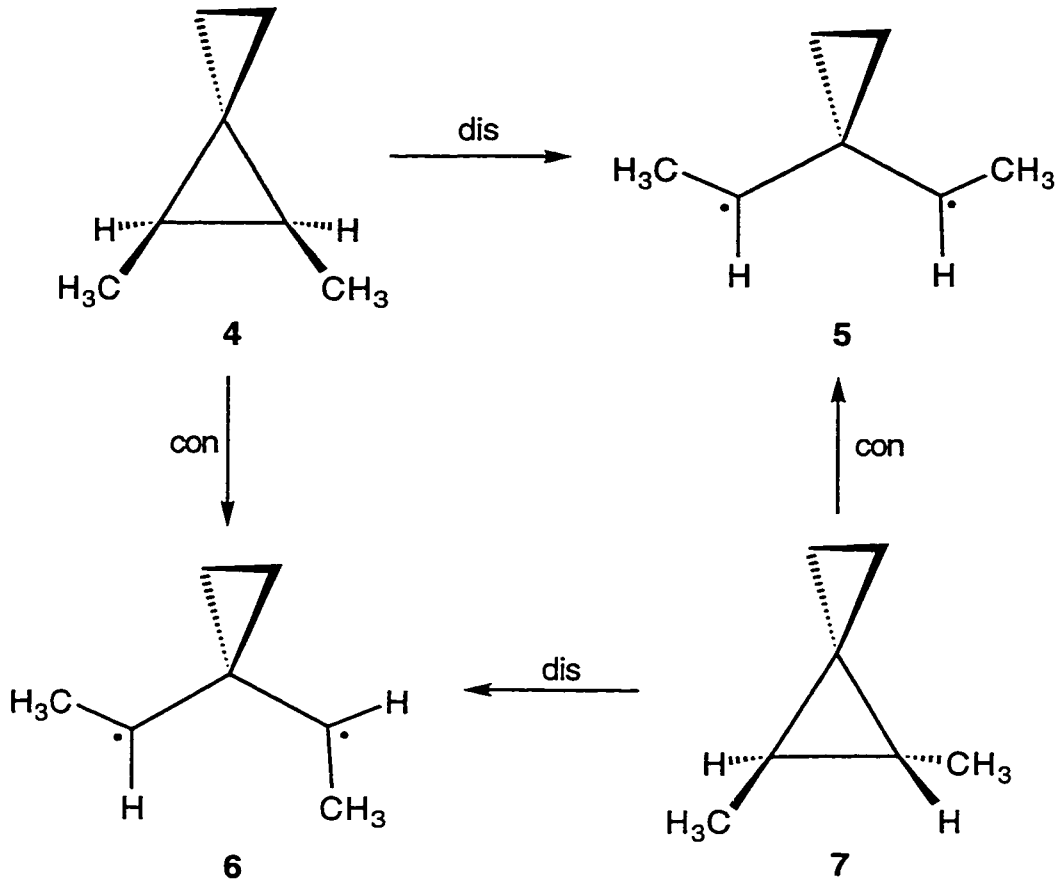


Figure 5.1. Diradicals formed by con- and disrotatory ring opening of *cis*- and *trans*-1,2-dimethylspiropentane.

(0,0) (0,90)

Figure 5.2. Idealized (0,0) and (0,90) conformations of trimethylene.

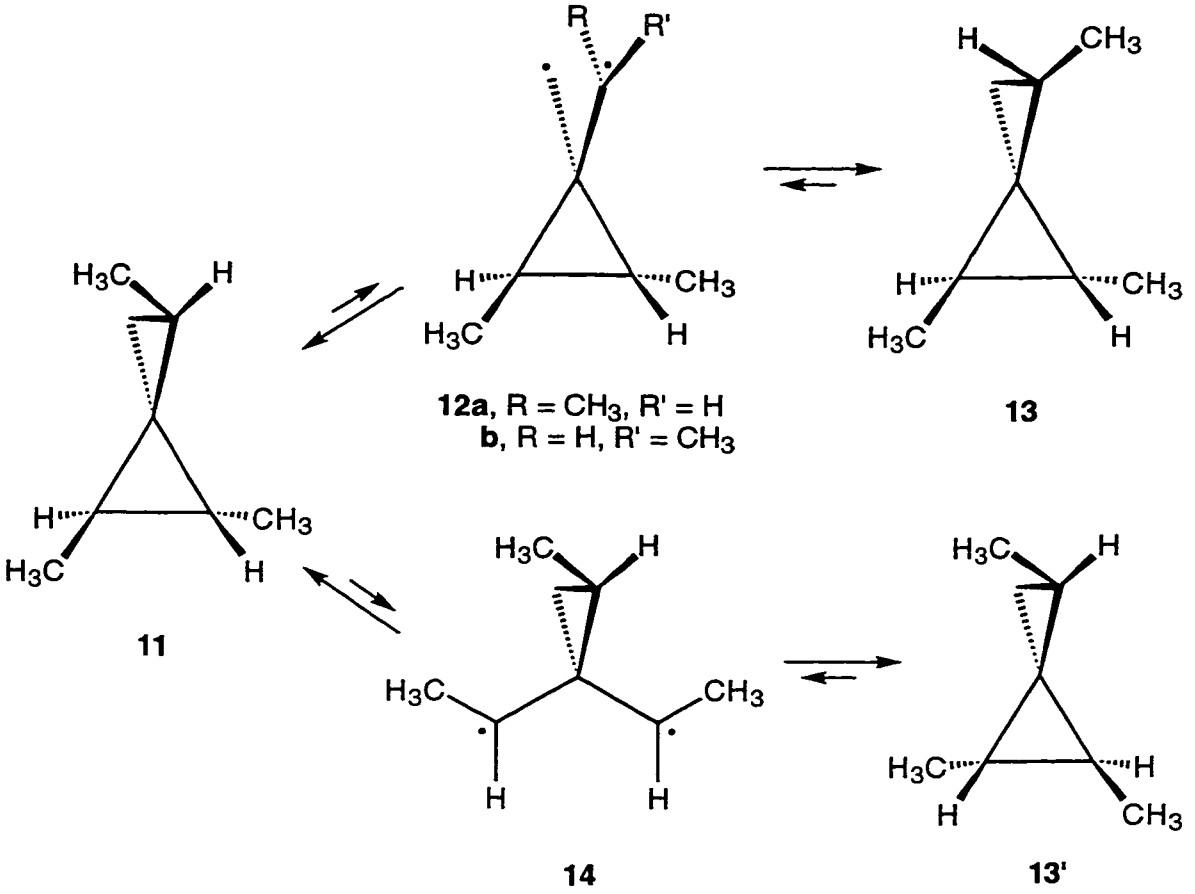
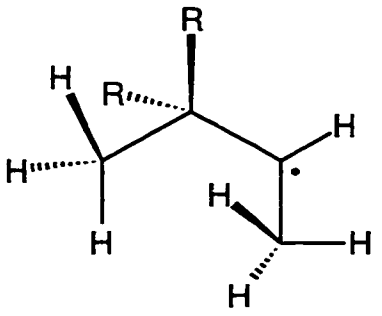
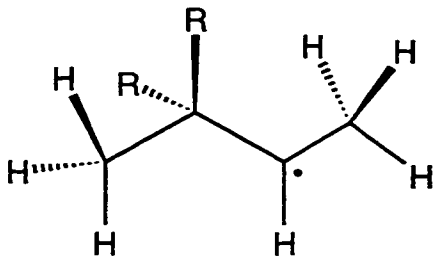


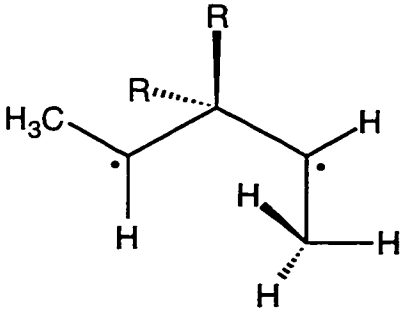
Figure 5.3. Pathway for stereomutation of *trans*-1,2,4-trimethylspiropentane **11** to **13** by cleavage of the bond between C-4 and C-5 and to **13'**, the enantiomer of **13**, by conrotatory cleavage of the bond between C-1 and C-2 in **11**.



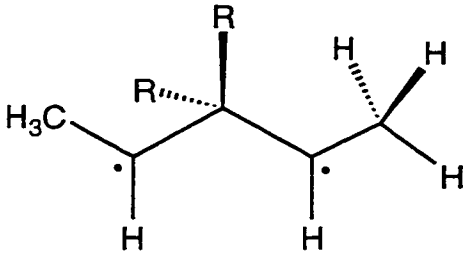
15a, R = H
b, R = F
c, R = SiH_3
d, R-R = H_2C-CH_2



16a, R = H
b, R = F
c, R = SiH_3
d, R-R = H_2C-CH_2



17a, R = H
b, R = F
c, R = SiH_3
6, R-R = H_2C-CH_2



18a, R = H
b, R = F
c, R = SiH_3
5, R-R = H_2C-CH_2

Figure 5.4. *s-cis* (**15**) and *s-trans* (**16**) monoradical and *s-cis*, *s-trans* (**17** and **6**) and *s-trans*, *s-trans* (**18** and **5**) diradical conformations.

Chapter 5 Notes

1. Review: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981, pp. 94 - 104.

2. Gilbert, J. C. *Tetrahedron* **1969**, *25*, 1459.

3. Gajewski, J. J.; Burka, L. T. *J. Am. Chem. Soc.* **1972**, *94*, 8857.

4. (a) Gajewski, J. J. *Chem. Commun.* **1967**, 920; (b) Gajewski, J. J. *J. Am. Chem. Soc.* **1970**, *92* , 3688.

5. (a) Gajewski, J. J.; Chang, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 7542; (b) Gajewski, J. J.; Weber, R. J.; Chang, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2100.

6. Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

7. (a) Getty, S. J.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2085; (b) Baldwin, J. E.; Yamaguchi, Y.; Schaefer, H. F., III *J. Phys. Chem.* **1994**, *98*, 7513; (c) Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc*, **1997**, *119*, 5251. (d) Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc*, **1997**, *119*, 5253. References to earlier *ab initio* calculations and to experimental studies of cyclopropane stereomutations are contained in these four papers.

8. See, for example, Olah, G. A.; Reddy, P. V.; Prakash, G. K. S. in *The Chemistry of the Cyclopropyl Group*, Rappoport, Z., Ed.; John Wiley and Sons: New York, 1995; Vol. 2, pp 813-859.

9. (a) The C-Si bonds in 2,2-disilyltrimethylene, which are much better hyperconjugative electron donors than C-H bonds at C-2 in trimethylene, have been calculated to enhance greatly the preference for conrotatory ring opening of

1,1-disilylcyclopropane, relative to the hydrocarbon. (b) Skancke, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 7079.

10. (a) Getty, S. J.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, **1994**, *116*, 1521; (b) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc. Faraday Trans.* **1994**, *90,* 1689; (c) Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, **1994,** *116*, 5425.

11. Tian, F; Lewis, S. B.; Bartberger, M. D.; Dolbier, W. R., Jr.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 6187.

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

13. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian 94, Revision B.3, Gaussian, Inc., Pittsburgh PA, 1995.

14. Review: Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.,* **1996**, *29*, 67.

15. Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

16. Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O., MOLCAS-3, University of Lund, Sweden

17. As is also the case on the (2/2)CASSCF reaction path of lowest energy for ring opening and closure of cyclopropane,[7] the lowest frequency mode in this C_S

intermediate corresponds to a symmetry-breaking rotation of the two methylene groups in the same direction. Formation of this intermediate by deviation from a purely conrotatory path allows the "inward" rotating hydrogens on the methylene groups to minimize their steric compression by avoiding the (0,0) geometry and passing sequentially through the plane of the carbon atoms.

18. Johnson, W. T. G.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 5930.

19. Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838.

20. The energy difference between the (0,0) and (0,90) conformations of trimethylene is 1.2 kcal/mol at the SD-CI level[7a] and 1.7 kcal/mol at CASPT2; Hrovat, D. A.; Borden, W. T., unpublished results.

21. Johnson, W. T. G.; Hrovat, D. A.; Skancke, A.; Borden, W. T. *Theor. Chem. Acc.,* **1999**, *102*, 207.

22. Walton, J. C. *Magn. Reson. Chem.* **1987**, *25*, 998.

23. Our calculations do indeed find that two-electron, hyperconjugative donation from the C-C bonds of a cyclopropane ring into the empty p-π AO of a carbocation is highly stabilizing and to about the same extent as hyperconjugative donation from the C-Si bonds of two geminal silyl groups. Since our calculations also find that the cyclopropane ring bonds in **2-(0,0)** are much poorer hyperconjugative electron donors than the geminal C-Si bonds in the (0,0) conformation of 2,2-disilylpropane-1,3-diyl, this difference between the relative electron donating abilities of cyclopropane and geminal C-Si bonds in carbocations and in 1,3-diradicals presents an apparent paradox. We believe that the resolution of this paradox is that hyperconjugative electron donation in **2-(0,0)** necessitates charge separation; whereas, even in 2,2-disilylpropane, the C-Si bonds are highly polarized, with positive charges on silicon and a negative charge at the carbon to which they are attached. Consequently, hyperconjugative stabilization in

2,2-disilylpropane-1,3-diyl largely involves delocalization of negative charge, already at C-2 in 2,2-disilylpropane, to C-1 and C-3, rather than creation of charge separation, as required for hyperconjugative electron donation in **2-(0,0)**.

24. As predicted,[10c] the ground state of a cyclic derivative of 2,2-difluorotrimethylene has been shown experimentally to be a singlet [Adam, W.; Borden, W. T.; Burda, C.; Foster, H.; Heidenfelder, T.; Heubes, M.; Hrovat, D. A.; Kita, F.; Lewis, S. B.; Scheutzow, D.; Wirz, J. *J. Am. Chem. Soc.*, **1998**, *120*, 593.

25. (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99,* 4587; (b) Borden, W. T. in Borden, W. T., Ed., *Diradicals*, Wiley-Interscience, New York, 1982, pp. 1-72; (c) Borden, W. T. in Schleyer, P. von R., Ed., "The Encyclopedia of Computational Chemistry" Wiley, 1998, pp. 708-22; (d) Borden, W. T. in Lahti, P. M. Ed., "Magnetic Properties of Organic Materials", Marcel Dekker, New York, 1999, in press.

26. Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.*, **1983**, *105*, 284.

27. Based on the energies in Table 5.2, it seems likely that the (0,0) diradical geometries, **5** and **6**, would be found to be closer than the (2/2)CASSCF conrotatory transition structures, **5-con** and **6-con**, to the geometries of the CASPT2 conrotatory transition states. Unfortunately, analytical gradients have not yet been implemented in MOLCAS for CASPT2 wavefunctions; so currently, this conjecture cannot be easily verified.

28. Even though the (2/2)CASSCF geometries of **5-con** and **6-con** are probably not the transition structures for conrotatory ring opening of, respectively, **7** and **4** on the CASPT2 surface,[27] comparison of the enthalpies of **5-con** and **6-con** is more meaningful than comparison of the enthalpies of diradicals **5** and **6**, since the former diradical has one more imaginary vibrational mode than the latter.

29. In order to compute the actual ratios of double to single rotations in the stereomutations of **4** and **7**, reaction dynamics calculations would be necessary.

Dynamics calculations on the stereomutation of cyclopropane have found that molecules which undergo disrotatory ring opening do not, as predicted by transition state theory, contribute to net monorotation by undergoing preferential conrotatory closure.[7c,d] Instead, dynamical effects favor molecules which undergo disrotatory ring opening contributing to double rotation by undergoing disrotatory closure

30. The stabilization associated with the long-range attraction between an *s-cis* methyl group at C-1 and the nonbonding p-π AO at C-3 in **17** can be reduced by rotating the *s-cis* methyl group such that the π combination of C-H bonds points away from the C-3 radical center. For both R = H and R-R = H_2C-CH_2, rotating the *s-cis* methyl group in this fashion costs ca. 1.5 kcal/mol; and for R = SiH_3, this rotation raises the energy by 2.6 kcal/mol. For R = F, rotating the *s-cis* methyl group costs only 0.4 kcal/mol, because in **17b** the long-range interaction between the *s-cis* methyl group at C-1 and the nonbonding p-π AO at C-3 is repulsive rather than attractive.[10b]

Bibliography

1. Adam, W.; Borden, W. T.; Burda, C.; Foster, H.; Heidenfelder, T.; Heubes, M.; Hrovat, D. A.; Kita, F.; Lewis, S. B.; Scheutzow, D.; Wirz, J. *J. Am. Chem. Soc.* **1998**, *120*, 593.

2. Adam, W.; Platsch, H. *J. Am. Chem. Soc.* **1989**, *111*, 6896.

3. Allan, M. *J. Electron Spectrosc. Relat. Phenom.* **1989**, *48*, 219.

4. Allan, M. *Helv. Chim. Acta* **1982**, *65*, 2008.

5. Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O., MOLCAS-3, University of Lund, Sweden.

6. Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

7. Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.

8. Apeloig, Y.: Nakash, M. *J. Am. Chem. Soc.* **1994**, *116*, 10781.

9. Asmis, K. R.; Allan, M. *J. Chem. Phys.* **1997**, *106*, 7044.

10. Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838.

11. Baldwin, J. E.; Ollerenshaw, J. *J. Org. Chem.*, **1981**, *46*, 2116.

12. Baldwin, J. E.; Yamaguchi, Y.; Schaefer, H. F., III *J. Phys. Chem.* **1994**, *98*, 7513.

13. Barone, V.; Minichino, C.; Faucher, H.; Subra, R.; Grand, A. *Chem. Phys. Lett.* **1993**, *205*, 324.

14. Benson, S. W. *J. Chem. Ed.* **1965**, *42*, 502.

15. Benson, S. W.; "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; pp 63-65.

16. Bertz, S. H.; Cook, J. M.; Gawish, A.; Weiss, U.; *Org. Synth. Coll. Vol. VII* **1990**, 50.

17. Borden, W. T. *Chem. Revs.* **1989**, *89*, 1095.

18. Borden, W. T., Ed., *Diradicals*, Wiley-Interscience, New York, 1982, pp. 1-72.

19. Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

20. Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

21. Borden, W. T. in Lahti, P. M. Ed., "Magnetic Properties of Organic Materials", Marcel Dekker, New York, 1999, in press.

22. Borden, W. T. in Schleyer, P. von R., Ed., "The Encyclopedia of Computational Chemistry" Wiley, 1998, pp. 708-22.

23. Borden, W. T. *Synlett*, **1996**, *115*, 711.

24. Branan, B. M.; Paquette, L. A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 774.

25. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857.

26. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

27. Bulliard, C.; Allan, M.; Smith, J. M.; Hrovat, D. A.; Borden, W. T.; Grimme, S. *Chem. Phys.* **1997**, *225*, 153.

28. Camps, P.; Font-Bardia, M.; Pérez, F.; Solans, X.; Vásquez, S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 912.

29. Camps, P.; Iglesias, C.; Rodríguez, M. J.; Grancha, M. D.; Gregori, M. E.; Lozano, R.; Mirands, M. A.; Figueredo, M.; Linares, A. *Chem. Ber.* **1988**, *121*, 647.

30. Carpenter, F. H. *J. Am. Chem. Soc.* **1948**, *70*, 2964.

31. Coolidge, M. B.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2354.

32. Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1979**, *101* 2245.

33. Coms, F. D.; Dougherty, D. A., *J. Am. Chem. Soc.*, **1989**, *111*, 6894.

34. Danen, W. C., *J. Am. Chem. Soc.* **1972**, *94*, 4835.

35. Deycard, S.; Hughes, L.; Lusztsyk, J.; and Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 4954.

36. Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc*, **1997**, *119*, 5251.

37. Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533.

38. Ellison, G. B.; Davico, G. E.; Bierbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrom., Ion Proc.* **1996**, *156*, 109.

39. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian 94, Revision B.3, Gaussian, Inc., Pittsburgh PA, 1995.

40. Fujimori, K. in "Organic Peroxides"; Ando, W., Ed. John Wiley & Sons: New York, 1992, pp. 319-85.

41. Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981, pp. 94 - 104.

42. Gajewski, J. J.; Burka, L. T. *J. Am. Chem. Soc.* **1972**, *94*, 8857.

43. Gajewski, J. J.; Chang, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 7542.

44. Gajewski, J. J. *Chem. Commun.* **1967**, 920.

45. Gajewski, J. J. *J. Am. Chem. Soc.* **1970**, *92* , 3688.

46. Gajewski, J. J.; Weber, R. J.; Chang, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2100.

47. Getty, S. J.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2085.

48. Getty, S. J.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, **1994**, *116*, 1521.

49. Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc. Faraday Trans.* **1994**, *90,* 1689.

50. Gilbert, J. C. *Tetrahedron* **1969**, *25*, 1459.

51. Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.

52. Greenberg, A., and Liebman, J. F., *Strained Organic Molecules*, Academic Press, New York, 1978, pp. 91-3.

53. Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127.

54. Halton, B., and Banwell, M. G. in "The Chemistry of the Cyclopropyl Group", Rappoport, Z., Ed., John Wiley & Sons: New York, 1987, Vol. 1, Part 2, p. 1251.

55. Hamilton, J. G.; Palke, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 4159.

56. Hammons, J. H.; Coolidge, M. B.; Borden, W. T. *J. Phys. Chem.* **1990**, *94*, 5468.

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

58. Hehre, W. J., *J. Am. Chem. Soc.* **1973**, *95*, 2643.

59. Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* , **1988**, *110*, 2681.

60. Hoffmann, H. M. R.; El-Khawaga, A. M.; Oehlerking, H.-H. *Chem. Ber.* **1991**, *124*, 2147.

61. Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

62. Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710.

63. Hrovat, D. A.; Borden, W. T. *J. Phys. Chem.* **1994**, *98*, 10460.

64. Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc*, **1997**, *119*, 5253.

65. Hrovat, D. A.; Sun, H.; Borden, W. T. *Theochem* **1988**, *163*, 51.

66. Johnson, W. T. G.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 5930.

67. Johnson, W. T. G.; Hrovat, D. A.; Skancke, A.; Borden, W. T. *Theor. Chem. Acc.* **1999**, *102*, 207.

68. Kolesov, V. P., and Kozina, M. P. *Russ. Chem. Rev.*, **1986**, *55*, 912.

69. Kumar, A.; Lichtenhan, J. D.; Critchlow, S. C.; Eichinger, B. E.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 5633.

70. Liebman, J. F., and Greenberg, A., *Chem. Rev.*, **1976**, *76*, 311, p. 324.

71. Lien, M. H.; Hopkinson, A. C. *J. Comput. Chem.* **1985**, *6*, 274.

72. McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1971**, *3*, 359.

73. Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

74. Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 1912.

75. Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114,* 8682.

76. Nicolaides, A.; Smith, J. M.; Kumar, A.; Barnhart, D. M.; Borden, W. T. *Organometallics* **1995**, *14*, 3475.

77. Olah, G. A.; Reddy, P. V.; Prakash, G. K. S. in *The Chemistry of the Cyclopropyl Group*, Rappoport, Z., Ed.; John Wiley and Sons: New York, 1995; Vol. 2, pp 813-859.

78. Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman & Hall, New York, 1986.

79. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *S10*, 1.

80. Radom, L; Paviot, J.; Pople, J. A.; Schleyer, P. v. R. *J. C. S., Chem. Comm.* **1974**, 58.

81. Radziszewski, J. G.; Yin, T.-K. Miyake, F.; Renzoni, G. E.; Borden, W. T.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3544.

82. Radziszewski, J. G.; Yin, T.-K.; Renzoni, G. E.; Hrovat, D. A.; Borden, W. T.; Michl, J. *J. Am. Chem. Soc.* **1993**, *115*, 1454.

83. Renzoni, G. E.; Yin, T.-K.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 7121.

84. Renzoni, G. E.; Yin, T.-K.; Miyake, F.; Borden, W. T. *Tetrhedron* **1986**, *42*, 1581.

85. Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Gutman, D; Kransoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847

86. Sherrill, C. D.; Seidl, E. T.; Schaefer, H. F. *J. Phys. Chem.* **1992**, *96*, 3712.

87. Skancke, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 7079.

88. Smith, J. M.; Hrovat, D. A.; Borden, W. T.; Allan, M.; Asmis, K. R.; Bulliard, C.; Haselbach, E.; Meier, U. C. *J. Am. Chem. Soc.* **1993**, *115*, 3816.

89. Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275.

90. Tian, F; Lewis, S. B.; Bartberger, M. D.; Dolbier, W. R., Jr.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 6187.

91. Walton, J. C., *Magn. Reson. Chem.* **1987**, *25*, 998.

92. Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282.

93. Weiss, U.; Edwards, J. M. *Tetrahedron Lett.* **1968**, 4885.

94. Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

95. Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, **1994**, *116*, 5425.

Vita

William Johnson was born in Spartanburg, South Carolina where he attended the Spartanburg Day School, and was taught Chemistry by Dr. Alfred Finkelstein. He was a National Merit Scholar, and graduated as the salutatorian of his class in 1989. He attended Harvey Mudd College for the next for four years where he was instructed in organic chemistry by Prof. Philip Myrhe. He graduated with his Bachelor of Science in Chemistry degree in 1993, and his thesis project, "Studies of the Stereoselectivity of Substituted Claisen Rearrangements," was supervised by Prof. Bill Daub. The summer of that year, he began his doctoral studies with Prof. Wes Borden at the University of Washington. He was the Bernard and Claudine Nist Graduate Student Fellow in 1993. He graduated with his Ph. D. in 1999, and continued on to the University of Minnesota, Minneapolis, as a post-doctoral fellow working with Prof. Chris Cramer.