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Pyramidalized Alkenes

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Contents

I. Introduction

Pyramidalized alkenes are molecules containing C–C double bonds in which one or both of the doubly bonded carbons do not lie in the same plane as the three atoms attached to it. If, even at geometries where the doubly bonded carbons are constrained to be planar, the two faces of the double bond are nonequivalent, the probability of the doubly bonded carbons being exactly planar at the equilibrium geometry is essentially zero. However, the degree of pyramidalization may be so slight as to be undetectable experimentally. This review deals with alkenes in which the amount of pyramidalization is large enough to have significant structural, spectroscopic, and chemical consequences.

Wes Borden was born in New York City on October 13, 1943, and received his B.A. degree from Harvard University. After spending a year as a Fulbright Fellow in Cambridge, England, studying molecular orbital theory with H. C. Longuet-Higgins, Professor Borden returned to Harvard for his graduate studies. There he worked with Professor E. J. Corey and received his Ph.D. in 1968. After five additional years as an Assistant Professor at Harvard, Professor Borden joined the Chemistry Department at the University of Washington as an Associate Professor and was promoted to the rank of Professor in 1977. Professor Borden's research encompasses both experimental and computational chemistry. His research group is involved in the synthesis and study of theoretically interesting organic molecules and in the application of ab initio molecular orbital calculations to the understanding and prediction of the structure and reactivity of organic and organometallic molecules. Professor Borden's research has been recognized by awards from the Sloan and Guggenheim Foundations, the Eli Lilly Co., and the Japanese Society for the Promotion of Science. He has been a Visiting Professor at Princeton University and at the Institute for Molecular Science in Okazaki, Japan. His nonscientific interests include ikebana, chado, other aspects of traditional Japanese culture, hiking, and racketball.

Pyramidalization of the doubly bonded carbons occurs in *trans*-cycloalkenes and in torsionally strained bridgehead olefins in order to increase the overlap between the atomic orbitals that form the "π" part of the double bond.[1,2] Torsionally strained, bridgehead alkenes have been reviewed[3] and will not be discussed again here. Instead, this review focuses on pyramidalized alkenes, like the one shown schematically in Figure 1, in which the atomic orbitals that form the "π" bond are perfectly aligned, so that torsional strain is absent.

Alkenes in which the doubly bonded carbons are pyramidalized are obviously related to alkynes in which the atoms attached to the triply bonded carbons deviate from collinearity with them. However, pyramidalized alkenes have a much shorter experimental history than bent alkynes. Although a book reviewing the chemistry of 1,2-dehydrobenzene and other bent cycloalkynes was published in 1967,[4] it was not until a year later that

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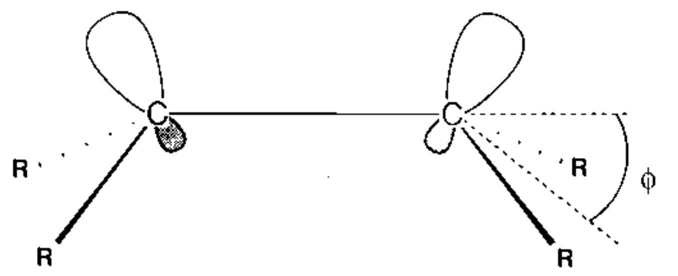


Figure 1. Schematic representation of a pyramidalized alkene.

Weinshenker and Greene[5] reported the synthesis of the first pyramidalized alkene. Many of the molecules discussed in this review have been prepared only during the past decade.

Much of the literature through 1979 has been discussed in the excellent review of bridgehead alkenes by Szeimies.[3a] The present review covers the literature on pyramidalized alkenes through 1987, and some of the developments published in 1988 are also discussed. The literature coverage of highly pyramidalized alkenes in this review is intended to be thorough, but the coverage of alkenes with only modest amounts of pyramidalization is considerably less exhaustive.

II. Theoretical Studies of Alkene Pyramidalization

In discussing pyramidalized alkenes, it is convenient to define a pyramidalization angle, ϕ. As shown in Figure 1, ϕ is the angle between the plane containing one of the doubly bonded carbons and the two substituents (R) attached to it and the extension of the double bond. From the bond angles, R–C–R and R–C–C, about the doubly bonded carbon, the pyramidalization angle, ϕ, can be obtained from the formula[6]

$$\cos \phi = -\cos (\text{R–C–C})/[\cos \tfrac{1}{2}(\text{R–C–R})]$$

If the orbitals on carbon that form the C–H bonds followed the motions of the four hydrogens, one would expect the p orbitals of the C–C π bond to be transformed into hybrids by pyramidalization. As shown in Figure 1, these hybrid orbitals are not as well aligned for π bonding as pure p orbitals. Thus, pyramidalization is anticipated to result in a weakening of the C–C double bond.

As expected, the ab initio calculations on ethylene found pyramidalization to weaken and, hence, lengthen the C–C double bond.[6] However, population analyses showed that the orbitals of the C–H bonds do not follow perfectly the motions of the hydrogens. The calculations also found anti pyramidalization to be less energetically costly than the syn mode of pyramidalization, which is shown in Figure 1. This computational result was shown to be in accord with an analysis of the mixing that occurs between filled and empty orbitals of planar ethylene upon pyramidalization.

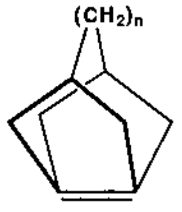
A. Comparison with Alkyne Bending

Houk and co-workers have offered a similar rationalization of their computational finding that the trans mode of bending of acetylene is considerably more facile than the cis mode.[7] They attributed the experimental preference for the trans mode of addition of nucleophiles to acetylene to the preferred trans bending of acetylene in the transition state. They also pointed out that an important contributor to the greater reactivity toward nucleophilic addition of acetylene compared to ethylene is the fact that trans bending of acetylene is considerably easier than anti pyramidalization of ethylene.

However, in contrast to the significantly greater ease of bending acetylene in a trans fashion, compared to pyramidalizing ethylene in an anti mode, cis bending of acetylene has a force constant about 25% greater than that for syn pyramidalization of ethylene.[8] As a result, a syn-pyramidalized alkene with a pyramidalization angle, ϕ, at both carbons will have only about 80% of the strain localized in its double bond as a comparably cis-bent alkyne has in its triple bond.

Houk and co-workers also found that bending acetylene results in a more rapid decrease in the LUMO energy than pyramidalizing ethylene. They rationalized this computational finding on the basis of the closer energetic proximity in acetylene than in ethylene of the σ^* and π^* orbitals that are mixed. In contrast, in both molecules the energy of the HOMO was found to be much less affected by molecular distortion.

Hrovat and Borden found the same effect—a dramatic lowering of the energy of the LUMO and a much smaller raising of the energy of the HOMO with increasing ϕ—in their calculations on the lower members of a homologous series of pyramidalized alkenes (1) and on the unconstrained bicyclic reference compound (2).[9] Hrovat and Borden rationalized the difference in the computed behavior of the HOMO and LUMO energies on double-bond pyramidalization in terms of the changes in the hybridization and overlap of the AOs that comprise these two MOs.



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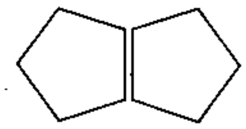


2

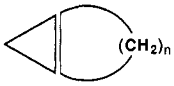
This predicted difference should, in principle, be capable of confirmation by measurement of the ionization potentials and electron affinities of this series of pyramidalized alkenes, as has been done already for some bent acetylenes.[10] In addition, according to frontier orbital theory, the larger lowering of the LUMO energy should, as in the case of bent acetylenes,[8] enhance the reactivity of pyramidalized alkenes toward nucleophiles more than toward electrophiles. Finally, the expected decrease in the HOMO–LUMO energy gap with increasing pyramidalization angle should result in a concomitant shift of the $\pi \rightarrow \pi^*$ transition toward longer wavelengths.

Experimental support for the last of these predictions has been obtained from measurements made on 1, n = 2, which shows a long-wavelength UV absorption.[11] The synthesis, matrix isolation, and spectroscopy of this pyramidalized alkene are described in section V.B of this review.

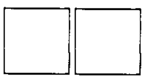
B. Predicted Pyramidalization in Bicyclo[*n*.1.0]alk-1(*n*+2)-enes

Certainly one of the most interesting general predictions to emerge from calculations is that the ease of pyramidalization of an alkene depends critically on the bond angles at the doubly bonded carbons in the planar molecule.[12] Model calculations on ethylene by Wagner and co-workers showed that when the H–C–C bond angles in the planar molecule are all deformed to values of <100°, pyramidalization becomes favorable. This result can be understood on the basis of mixing between a low-lying, unfilled orbital of the strained σ skeleton and the filled π orbital of the double bond.[13] However, Wiberg has pointed out that pyramidalization in an alkene in which the R–C–C bond angles are constrained to be small also has the effect of reducing toward a more normal value the large R–C–R angle in the planar molecule.[14]

The model calculations on ethylene suggest that, in molecules like bicyclo[1.1.0]but-1(3)-ene (**3**), bicyclo[2.1.0]pent-1(4)-ene (**4**), and bicyclo[2.2.0]hex-1(4)-ene (**7**), a planar geometry might not be a minimum but instead a transition state, connecting two equivalent geometries with syn-pyramidalized olefinic carbons. This was, in fact, found to be the case for **3** and **4** by Wagner and co-workers. Subsequent calculations of higher quality have been performed on **3**[9,15,16] and on **4**,[15] and these later calculations have confirmed the previous results.



3, n = 1
4, n = 2
5, n = 3
6, n = 4



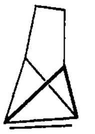
7

In contrast to **3** and **4**, **7** was predicted to have a planar geometry but a small force constant for pyramidalization.[12] Once again, the finding of a planar geometry for **7** was confirmed by subsequent calculations.[9,15] Apparently, the presence of a three-membered ring in a bicycloalkene is required in order for a planar geometry to be a transition state rather than an equilibrium geometry.

Calculations performed by Wagner and co-workers[12] and by Wiberg and co-workers[15] found a nonplanar equilibrium geometry for **5**, but a barrier to planarity of only 1–3 kcal/mol. The drawing of the calculated equilibrium geometry of **6** published by Wiberg and co-workers[15] also shows the doubly bonded carbons to be pyramidalized. However, the six-membered ring is in a boat conformation, so that, unlike the case in **3**–**5** or **7**, the two faces of the double bond are not equivalent. Therefore, there is no symmetry reason to expect a planar geometry at the doubly bonded carbons in **6** to be a stationary point, either a minimum or a transition state.

Experimentally, **3** and **4** have not been isolated, so no structural information about them is available. Polycyclic derivatives of **3** and **4** have been prepared by Szeimies and co-workers,[3a] and their chemistry is reviewed in sections VII and VIII. The fact that **3** and **4** are predicted to be pyramidalized suggests that the introduction of bridging groups, which preclude planarity, should introduce but little additional strain. A computational test of this qualitative prediction has been performed on tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene (**8**).[9] The results, which are in accord with this qualitative prediction, are discussed in section VIII.

Bicyclo[2.2.0]hex-1(4)-ene (**7**) has been prepared and studied by Wiberg and co-workers, and its chemistry has been reviewed by him.[17] Although this alkene has proved too reactive for a structural study, the small force constant calculated for pyramidalization would again be expected to permit the synthesis of molecules containing highly pyramidalized bicyclo[2.2.0]hex-1(4)-ene moieties. Calculations of the relative heats of hydrogenation of **7** and of cubene (**9**) support this conjecture,[9] and the results of these calculations are discussed in section VI.



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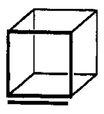

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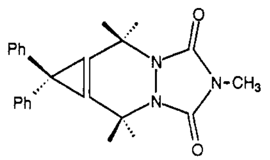


10

Direct experimental evidence for pyramidalization at the doubly bonded carbons in a bicyclo[*n*.1.0]alk-1-(*n*+2)-ene has been found in **10**,[18] which may be regarded as a highly substituted derivative of **6**. The chemical stability of **10**, which was attributed by Ando and co-workers to the bulky groups that surround the double bond and thus prevent it from reacting, allowed an X-ray structure determination to be performed. The X-ray structure revealed that the doubly bonded carbons in **10** are indeed pyramidalized, so that the flap angle between the two rings is not 180° but 162°. The X-ray structure shows the six-membered ring in **10** to be nearly planar; consequently, pyramidalization of the doubly bonded carbons apparently cannot be attributed to an environment of low symmetry.

C. Predicted Pyramidalization in Environments of Low Symmetry

Ab initio calculations by Morokuma and Wipff,[19] by Houk and co-workers,[20] and by Wiberg and co-workers[15] on norbornene and related molecules in which the two faces of the double bond are nonequivalent found substantial amounts of pyramidalization. Force field calculations[21,22] also predicted pyramidalization in the sense that minimizes steric interactions involving the doubly bonded carbons and the allylic carbons adjacent to them. Houk and co-workers[20] and Burkert[22] independently proposed that the calculated pyramidalization of the doubly bonded carbons is, in fact, nothing more than a classical torsional effect, which favors staggering of the bonds at adjacent carbons.

The experimental evidence for pyramidalization of doubly bonded carbons in the predicted sense, alternative explanations, and the effect of minimization of torsional interactions on the transition states for addition reactions to double bonds have all been reviewed by Houk.[23] Experimental and theoretical studies of sesquinorbornene, whose syn isomer exhibits a particularly large amount of pyramidalization at the doubly bonded carbons, are discussed in section IV of this review.

D. Calculation of Strain Energies Caused by Enforced Pyramidalization

Maier and Schleyer have defined olefin strain energy (OSE) as the difference in strain energy between an alkene and its hydrogenation product.[24] Thus, the OSE of a pyramidalized alkene should provide an excellent quantitative measure of the strain energy that results

TABLE I. Pyramidalization Angles (ϕ) and Olefin Strain Energies (kcal/mol) Calculated for Some Pyramidalized Alkenes[a]

alkene	ϕ,[b] deg	ab initio OSE[c]	MM2 OSE[d]	MNDO OSE[e]
1, $n = 1$	52.8	52.3	24.5	66.6
1, $n = 2$	40.8	37.4	18.2	46.9
1, $n = 3$	25.0, 25.2	17.7	9.8	30.8
3	39.8[f]	58.7		
7	0.0	40.0		
8	48.4[f]	66.8		
9	84.1	58.9		

[a] From ref 9. [b] From 3-21G SCF geometry optimizations. [c] From the difference between the 6-31G* calculated hydrogenation energy and that computed for 2. Two-configuration (TC) SCF energies were used for the alkenes, and SCF energies were employed for the alkanes. [d] From the difference in strain energies computed for the alkene and alkane. [e] From the difference between the calculated hydrogenation energy and that computed for 2. [f] The unusual geometry of this alkene makes the double bond, rather than its extension, more appropriate for defining the pyramidalization angle.

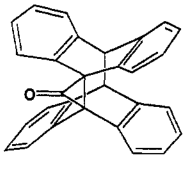
from the presence of a C–C double bond in an environment that does not easily accommodate the preferred geometry of this linkage. Maier and Schleyer reported MM1 calculations of the OSE of several pyramidalized alkenes.

In principle, the OSE of pyramidalized alkenes could be obtained by measuring their heats of hydrogenation and comparing them with the heats of hydrogenation of unstrained reference alkenes. In practice, highly pyramidalized alkenes are usually so reactive and/or available in such small quantities that such measurements are impossible. However, as discussed by Wiberg and co-workers,[15] heats of hydrogenation can be calculated fairly accurately at the ab initio SCF level with moderately sized basis sets. Since obtaining OSEs involves taking differences between heats of hydrogenation, systematic errors in calculated hydrogenation energies, introduced by finite basis set size and failure to include electron correlation, should tend to cancel. Thus, ab initio calculation of heats of hydrogenation provides a promising method for obtaining the OSEs of alkenes in general and of pyramidalized alkenes in particular.

Hrovat and Borden have discussed some of the advantages of using ab initio calculations, rather than semiempirical techniques or molecular mechanics, to obtain OSEs.[9] They performed ab initio calculations of the heats of hydrogenation of the lower members of the series of pyramidalized alkenes with structure 1 and obtained the OSEs by subtracting the calculated heat of hydrogenation of 2. In addition, the OSEs of 3 and 7–9 were computed. The OSEs, calculated with the 6-31G* basis set and a wave function that correlated the "π" electrons in the alkenes, are given in Table I, along with the pyramidalization angle, ϕ, at the 3-21G optimized geometry. The OSEs, obtained by molecular mechanics (MM2) and semiempirical quantum mechanics (MNDO) for 1, $n = 1$–3, are provided for comparison. The OSEs contained in Table I are each discussed in the relevant sections of this review.

III. 9,9′-Didehydrodianthracene (12) and Related Alkenes

Although Applequist and co-workers obtained evidence for the formation of 12 by treatment of 9-bromodianthracene with base,[25] the synthesis of this compound by Weinshenker and Greene[5] marked the first succsssful isolation of an alkene with a substantially pyramidalized double bond. The pyramidalized double bond in 12 was introduced by photochemical decarbonylation of cyclopropanone 11. The alkene was stable enough to isolate at room temperature, but heating to 80 °C in hexane effected its isomerization to 9,9′-bianthryl with a half-time of about 0.5 h.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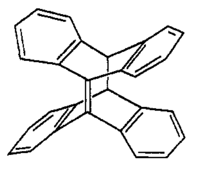
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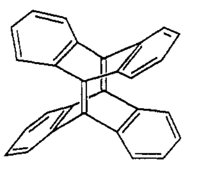

13

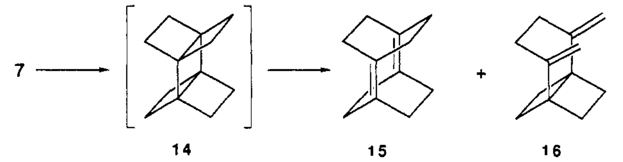
Greene and co-workers subsequently published an alternative synthesis of 12,[26] which involved dehydrobromination of 9-bromodianthracene, trapping the pyramidalized alkene formed with azide ion, converting the triazoline to the N-aminotriazoline, from which 12 was regenerated by oxidation with $Pb(OAc)_4$. The pyramidalized alkene could not be isolated directly from the dehydrohalogenation reaction, because the *tert*-butoxide base used was found to add to the pyramidalized double bond. This was the first experimental indication that pyramidalized alkenes are, in fact, unusually succeptible to nucleophilic addition reactions, as predicted by frontier orbital theory.

A. 9,9′,10,10′-Tetradehydrodianthracene (13)

The same reaction sequence was applied to the preparation of pyramidalized diene 13.[26] An X-ray structure of 13 found the lengths of the pyramidalized double bonds to be 1.35 Å and the pyramidalization angles, ϕ, to be 19.7°. How much of the pyramidalization in 13 is due to possible repulsion between the π clouds of the two double bonds is not clear, since crystal disorder precluded an accurate X-ray determination of ϕ in monoolefin 12.

B. Tricyclo[4.2.2.2^{2,5}]dodeca-1(2),5(6)-diene (15)

Whereas 13 may be viewed as two C–C double bonds attached at the ortho positions of four benzene rings, in 15 the double bonds are joined by four ethano bridges. Wiberg and co-workers isolated 15 from the dimerization of bicyclo[2.2.0]hex-1(4)-ene (7) in dilute solution.[27] The presumed double [2.2.2]propellane intermediate (14) was not observed, but 15 was accompanied by 16, another possible cleavage product of 14. On heating, 15 and 16 underwent equilibration via a Cope rearrangement. The temperature dependence of the equilibrium constant between 15 and 16 revealed that 15 is enthalpically favored over 16 by 4.7 kcal/mol but entropically disfavored by 15 eu.



14 15 16

An X-ray structure of 15[28] showed C–C double-bond lengths of 1.35 Å, as in 13,[26] a pyramidalization angle,

ϕ, of 27.3°, and a separation between the two double bonds of 2.395 Å. At this distance there should be a strong through-space interaction between the two double bonds, which would be expected to lead to the observation of two bands in the photoelectron (PE) spectrum of **15**. However, the actual PE spectrum showed only a single band at 8.6 eV.[27]

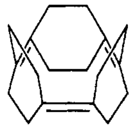
Wiberg and co-workers attributed this result to the interaction of the pyramidalized “π” bonds with the four suitably aligned σ bonds. This through-bond interaction has the opposite effect from the through-space interaction on the relative energies of the two possible symmetry combinations of the “π” bonds. Calculations by Wiberg and co-workers showed that, at the experimentally determined spatial separation between the two pyramidalized double bonds, the two effects are of equal size. Their cancellation results in the observation of just one band in the PE spectrum of **15** for both symmetry combinations of π bonds.

Wiberg and co-workers also investigated some of the chemistry of **15**.[27] Two observations were indicative of the unusual reactivity of each of the pyramidalized double bonds. First, tetrasubstituted alkenes do not usually undergo hydrogenation with Wilkinson's catalyst, but **15** does. Second, on exposure to molecular oxygen, mono- and diepoxides were formed. Wiberg and co-workers pointed out that the latter reaction appears to be a common one for molecules containing strained π bonds.

The photochemistry of **15** has also been studied.[29] No compelling evidence was found for transannular ring closure to afford double propellane **14**. Instead, the photoproducts were **16** and 1,2,5,6-tetramethylenecyclooctane.

C. Related Polyenes

McMurry has pointed out that, if **15** is viewed as being formed from two six-membered rings that are joined by double bonds at their 1,4 positions, a whole series of such hydrocarbons is possible, whose members differ only in the number of six-membered rings they contain.[30] McMurry and co-workers have reported the synthesis of the $n = 3$ (**17**)[30] and $n = 4$ (**18**)[31] members of this series, of which **7** and **15** may be considered, respectively, to be the $n = 1$ and $n = 2$ members.



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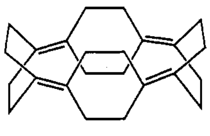
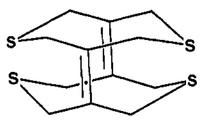


18

The synthesis of both **17** and **18** utilized titanium-induced coupling of a diketone precursor to introduce the final double bond and thus effect cyclization. The bond angles from the X-ray structure of **17**[30] give a pyramidalization angle, ϕ, of 7.0°. The PE spectrum of **17** revealed very little splitting of the π ionizations, thus indicating small interactions between the double bonds. In **18**[31] the cavity is large enough to accommodate an Ag(I) ion, and X-ray structures of both **18** and its square-planar complex with Ag(I) were obtained.

Schriver and Thomas have reported the synthesis of **19** by cesium cabonate promoted coupling of tetrakis(bromomethyl)ethylene with tetrakis(thiomethyl)ethylene.[32] Unfortunately, crystals suitable for X-ray diffraction could not be grown; so the geometry at the doubly bonded carbons is not known. Unlike diene **15**, which lacks the sulfur atom in each bridge, **19** was found to undergo photochemically induced intramolecular cycloaddition, which gave double [3.3.2]propellane **20**.



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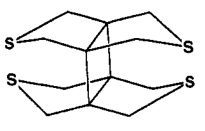

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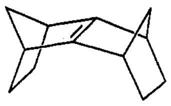
In **15** and in **17**–**19** the C–C double bonds all lie in a common symmetry plane. Alder and Sessions[33] and Angus and Johnson[34] have reported calculations on a series of homoconjugated, toroidal polyenes comprised of variable numbers of 1,4-cyclohexadiene rings oriented so that the C–C double bonds are perpendicular to the analogous plane of symmetry. The lower members of this series are predicted to be substantially pyramidalized and thus present interesting and challenging synthetic targets. McEwen and Schleyer have published calculations on trishomoaromaticity in these and related polyenes.[35]

McMurry and Swenson have attempted the synthesis of **21**,[36] an isomer of **15** in which the double bonds lie in orthogonal planes rather than in or orthogonal to the same plane. Titanium-induced coupling of the carbonyl groups of bicyclo[5.5.0]dodec-1(7)-ene-4,10-dione apparently led to the desired alkene; but, under the reaction conditions, **21** underwent a Cope rearrangement to afford **22**. Molecular mechanics calculations predict substantial pyramidalization of the double bonds in **21**. The ensuing strain is presumably responsible for the fact that the rearrangement of **21** to **22** was computed to be highly (22 kcal/mol) exothermic.

21 22

IV. Sesquinorbornenes and Related Alkenes

Because the two faces of the double bond are different in *syn*-sesquinorbornene (**23**), the doubly bonded carbons would not be expected to be exactly planar. In contrast, *anti*-sesquinorbornene (**24**) potentially possesses a C_2 axis of symmetry that lies along the C–C double bond. As a consequence of the equivalence of the two faces of the double bond, a planar equilibrium geometry at the doubly bonded carbons is at least a possibility for **24**.



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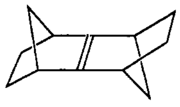

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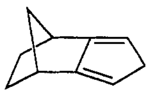


25

syn-Sesquinorbornene (**23**) and derivatives were prepared by Paquette and co-workers[37] during the course of a general study of long-range stereoelectronic control by norbornyl frameworks.[38] Reaction of isodicyclopentadiene (**25**) with various dienophiles gave mainly adducts with the *syn*-sesquinorbornene skeleton.[39] The adduct with phenyl vinyl sulfone was converted to **23** by reduction with sodium amalgam.

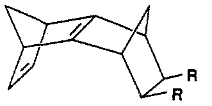
Paquette and Gleiter have rationalized the π-facial selectivity that is observed in the cycloaddition reactions of **25** on the basis of tilting of the lower of the two filled "π" orbitals of this diene.[37,38] It should be noted, however, that Brown and Houk have provided an alternative explanation, based on pyramidalization of the doubly bonded carbons of **25** in a mode that minimizes torsional interactions in the transition states for cycloaddition.[40] As discussed in section II.C of this review, Houk and co-workers have proposed that minimization of eclipsing interactions results in the pyramidalization of doubly bonded carbons both in ground states and in transition states.[23]

A. Structural Studies

X-ray studies performed on the anhydride and phenyl sulfone derivatives of **23** by Watson, Bartlett, and coworkers[41] showed that the doubly bonded carbons in these molecules are significantly pyramidalized. The flap angle between the planes of the two rings, to which the double bond is common, was found to be 162–164°, and the pyramidalization angles at the doubly bonded carbons ranged from 24 to 26°. Pyramidalizations in the same sense and of approximately the same magnitude have been observed in all of the derivatives of **23**[42] whose X-ray structures have been obtained to date.

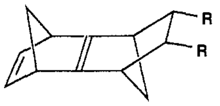
In contrast, Watson, Bartlett, and co-workers found the anhydride derivative[41] of *anti*-sesquinorbornene (**24**) to have a perfectly planar double bond. Although there are a few exceptions,[43] nearly planar alkene geometries have been the rule in the derivatives of **24** whose structures have been established[42a,b,d] and in the X-ray structure[44] of the parent hydrocarbon.[45]

The geometries of derivatives of *syn*-sesquinorbornadiene (**26**)[46–49] and *anti*-sesquinorbornadiene (**27**)[49] have also been obtained by X-ray crystallography. The central double bonds in the derivatives of **26** deviate from planarity even slightly more than those in comparable derivatives of **23**. The central double bond in the derivative of **27** that has been studied is nearly planar.



26, R = R = H

28, R-R = —



27, R = R = H

29, R-R = —

The syn (**28**) and anti (**29**) stereoisomers of sesquinorbornatriene have been prepared by Paquette, De Lucchi, and co-workers.[49] However, as yet, structural data on these hydrocarbons are unavailable. On the basis of the larger amount of double-bond pyramidalization found in derivatives of **26** compared to **23**, Paquette, De Lucchi, and co-workers have conjectured that **28** could represent the extreme example of π pyramidalization in a norbornene skeleton.

B. Spectroscopic Studies

The PE spectra of sesquinorbornenes **23** and **24** have been obtained.[50] Despite the fact that the double bond in the anti isomer (**24**) is planar, its first ionization potential (IP) is lower than that of the pyramidalized double bond in the syn isomer (**23**) by 0.22 eV. In solution, cyclic voltammetry also found **24** to have the lower oxidation potential by about the same amount.[50,51] The optical spectra of the derived radical cations have been obtained.[51]

Gleiter, Paquette, and co-workers have obtained the PE spectra of seaquinorbornadienes **26** and **27** and trienes **28** and **29**.[52] In each pair the anti isomer again had a slightly lower IP. These authors attributed this result to a larger hyperconjugative interaction between the central π bond and σ orbitals of the five-membered rings in the anti isomers than in the syn isomers. This interaction, which destabilizes the π orbital, is diminished in the syn isomers by pyramidalization of the central double bond. Also as discussed by these authors, because of the substantial difference between the IPs of di- and tetrasubstituted double bonds, the introduction of one or two additional double bonds has little apparent effect on the IPs of the central double bond in the sesquinorbornene skeleton.

Paquette, De Lucchi, and co-workers have discussed the effect of the introduction of additional double bonds on the ^{13}C chemical shifts of the carbons that form the central double bond in **23** and **24**.[49] In both isomers introduction of the first additional double bond causes a downfield chemical shift to 6–7 ppm, which is comparable to that observed on going from norbornene to norbornadiene. However, introduction of a second double bond to form **28** and **29** results in an additional 12–14 ppm downfield shift. Deuterium-induced ^{13}C chemical shifts have also been measured for trienes **28** and **29**.[52]

The ^{13}C chemical shift of δ 151.6 for the central carbons in **23**[53] is a little more than 2 ppm upfield from that in **24**[45] and about 12 ppm upfield from that in bicyclo[2.2.0]hexene (**7**).[17,54] Thus, the pyramidalization of the doubly bonded carbons in **23** does not seem to have much of an effect on their chemical shift. However, the Raman spectra of **23** shows the double-bond stretch at 1587 cm^{-1}, which is 16 cm^{-1} lower than that in planar **24**.[50] Both double-bond stretching frequencies are considerably lower than the 1664 cm^{-1} observed in the Raman spectrum of **7**[54] and the frequencies usually found in tetrasubstituted alkenes.[50]

C. Chemical Studies

Bartlett has reviewed some of the chemistry of **23** and **24**.[55] Reaction of the pyramidalized double bond in the syn isomer (**23**) with a variety of reagents, including diimide,[37] benzyne,[37] phenyl azide,[41,53] peracid,[53] and Br_2,[56] results in addition to the exo face of the double bond. The same stereochemistry of attack is observed in benzo derivatives of syn diene **26**.[53,57] The observed stereochemistry is certainly not surprising, since both electronic and steric factors would be expected to favor attack on the convex face of the pyramidalized double bond.

A striking exception to the general rule of exo addition was found by Bartlett and co-workers in the acetone-sensitized photohydrogenation of **23**.[58] This reaction, in which acetone acts as both a triplet sensitizer and a source of hydrogen atoms, leads to hydrogen addition with an endo:exo ratio of >10:1. This observation led Bartlett to propose that in the lowest triplet excited state **23** is pyramidalized in the opposite sense from in the ground state, and Bartlett provided a rationale for why this might be the case. Endo capture of hydrogen has also been found in a benzo derivative of syn diene **26**.[57]

Competition experiments between **23** and **24** performed by Bartlett and co-workers showed the syn isomer to react faster than the anti in concerted cycloadditions, but to be considerably less reactive toward ionic additions (Br_2 in CCl_4, HCl in ether, CH_3OH in aqueous acid).[59] As discussed by Bartlett and co-workers, the difference between the two sets of reactions appears to be related to the fact that the latter are reversible, and the equilibrium with the syn isomer (**23**) is much less favorable than with the anti isomer (**24**).[60]

Additions to the exo face of **23** result in severe compression between the endo hydrogens of the ethano bridges in the adducts, whereas steric compression between bridges is much less of a problem in the adducts of **24**. Therefore, the pyramidalized double bond in **23** may be intrinsically more reactive than the planar double bond in **24**, but the difference in intrinsic reactivity may be partially masked by steric interactions between the ethano bridges of **23** that develop in the transition states for its cycloaddition reactions.

Consistent with this postulate of retardation of the rates of cycloaddition reactions of **23** by steric effects is the observation that the benzo derivative of syn diene **26**, which lacks one pair of the endo hydrogens that are present in **23**, is more reactive than **23** toward epoxidation with peracid.[53] A similar difference between the benzo derivatives of **28** and **26** in their reactivity toward benzyne has also been noted.[37,53]

Increasing the number of double bonds in the *syn*-sesquinorbornene skeleton also increases the reactivity toward triplet oxygen. The benzo derivative of **26** yielded a mixture of epoxide and diketone products on exposure to triplet oxygen under conditions where **23** failed to react.[53] Triene **28** is so reactive to triplet oxygen that it must be handled in an inert atmosphere.[49] The anti isomer (**29**) is, however, apparently quite sensitive to oxygen, too.[49]

Nelsen and Teasely have reported that **23** is considerably more reactive than **24** toward ionic chain hydrogenation, initiated by protonation of the double bond and involving hydride abstraction from a dihydroaromatic.[61] Bartlett and co-workers have shown that both alkenes give observable cations on protonation in superacid but that the anti cation, formed from **24**, rearranges under conditions where the syn cation, formed from **23**, is stable.[62] The contrasting stabilities of the two cations were explained by the stereochemical difficulty of the latter cation utilizing a rearrangement pathway similar to that followed by the former. The syn cation was first generated by Paquette and co-workers, both in superacid and by solvolysis.[56]

D. Theoretical Studies

Computational studies of sesquinorbornene have been reviewed by Houk.[23] Obviously, the key points that need to be explained on the basis of computational results are the direction and magnitude of pyramidalization in the ground state of **23** and the apparently opposite mode of pyramidalization in the lowest triplet state.

Molecular orbital calculations that neglect overlap were found to predict nearly planar geometries for the double bond in **23**.[63,64] However, extended-Hückel[64] and ab initio[65] calculations, both of which include overlap, were found to predict correctly the sense of pyramidalization, not only in the ground state but also in the lowest triplet excited state of **23**. Ab initio calculations also correctly found **24** to be planar.[65,66]

Force field calculations gave the experimentally observed sense of pyramidalization for *syn*-sesquinorbornene (**23**) but predicted a pyramidalized equilibrium geometry for the anti isomer (**24**), too.[65,67] However, Houk and co-workers found that the barrier to planarity in **24** was only computed to be about 0.3 kcal/mol. This finding suggests that the potential for out-of-plane bending in **24** is quite soft, which may explain why nonplanar[43] geometries have been found in some derivatives.

Houk and co-workers showed that torsional interactions are responsible for the pyramidalization that is predicted in **23** by molecular mechanics.[65] When the torsional repulsions between the atoms around the double bond were set equal to zero, a planar geometry was found for the doubly bonded carbons. In quantum mechanical calculations inclusion of overlap is necessary in order to find eclipsing interactions to be repulsive. Thus, the planar geometry for **23** that is obtained by calculations that ignore overlap also is suggestive of torsional interactions as being responsible for the pyramidalization that is observed in **23**.

Some of the possible reasons why the double bond in **23** is more pyramidalized than that in norbornene have been discussed by Houk and co-workers.[65] They pointed out that the larger number of alkyl substituents attached to the double bond, the small R–C–C bond angles on both sides of the double bond, and the greater torsional asymmetry in **23** than in norbornene probably all contribute. The first two effects are probably also responsible for the softness of the potential for pyramidalizing the double bond in the anti isomer.

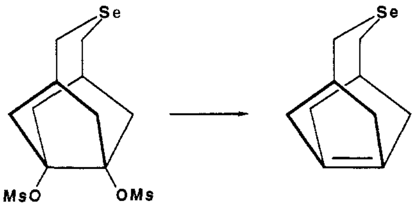
The opposite sense of double-bond pyramidalization predicted for the triplet state of **23** was attributed by Houk and co-workers to minimization of overlap between the p atomic orbitals of the π bond, which is repulsive in the lowest triplet state. Although minimization of overlap is accomplished in the lowest triplet state of ethylene by rotation about the C–C bond, appreciable rotation about the C–C double bond in **23** is clearly impossible. Houk and co-workers showed that pyramidalization of the olefinic carbons provides an alternative mode of reducing overlap in constrained alkenes like **23**. They also showed that substantial pyramidalization in the excited state of **23** is only sterically feasible in the sense opposite to the modest pyramidalization found in the ground state.

V. Tricyclo[3.3.n.0^{3,7}]alk-3(7)-enes (1) and Other Pyramidalized Derivatives of Bicyclo[3.3.0]oct-1(5)-ene (2)

The homologous series of alkenes **1** may be regarded as derivatives of bicyclo[3.3.0]oct-1(5)-ene (**2**) in which a sufficiently short bridge of methylene groups enforces pyramidalization of the double bond. It should be noted that the direction of enforced pyramidalization of the double bond in **1** is the opposite of that found to be favored in the bicyclo[3.3.0]oct-1(5)-ene moiety of *syn*-sesquinorbornene (**23**) and also opposite from that computed to be favored in **2**.[9] Consistent with the proposal that pyramidalization in **23** occurs to relieve unfavorable torsional interactions, a pyramidalized, C_{2v}, syn geometry for bicyclo[3.3.0]oct-1(5)-ene (**2**) was calculated to be lower in energy than a planar, C_{2h}, anti geometry.

A. 10-Selenatricyclo[3.3.3.0^{3,7}]undec-3(7)-ene (31)

This selenium derivative of the $n = 3$ alkene **1** was prepared by reduction of dimesylate **30** with sodium naphthalenide.[68] Alkene **31** proved stable enough to isolate at ambient temperature. The ^{13}C chemical shift of δ 150.7 for the doubly bonded carbons of **31** is not exceptional, since they appear only 4.7 ppm downfield from those in the unbridged reference compound (**2**).



30 31

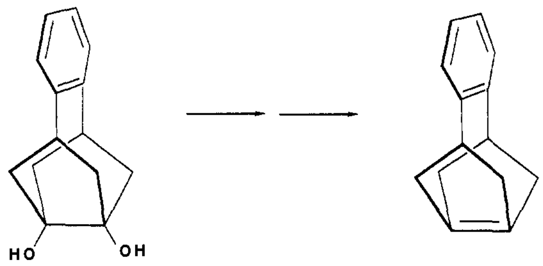
However, the double bond stretching frequency of 1625 cm^{-1} in **31** was found to be 60 cm^{-1} lower than that in **2**. Moreover, unlike the case in most tetrasubstituted alkenes, the double-bond stretch was visible in the IR spectrum of **31**. Double-bond pyramidalization in **31** is also presumably responsible for the fact that attempted TLC purification of **31** in the air led to the formation of the monoepoxide.

An X-ray structure of the 10-methylselenonium salt derived from **31** was obtained,[68] and the bond angle distortions in the five-membered rings and three-atom bridge were analyzed. Interestingly, the pyramidalization angles (20.3° and 12.3°) at the two doubly bonded carbons of **31** were found to be quite different, despite the fact that, as shown in Table I, 3-21G SCF calculations predict nearly identical values of ϕ for the two doubly bonded atoms in the $n = 3$ hydrocarbon.

It has been suggested that attraction between the selenonium moiety and the doubly bonded carbon syn to it results in flattening of this carbon and, hence, in the substantially smaller value of ϕ found at this carbon.[9] However, even at the anti carbon of the selenonium salt, the value of ϕ is considerably smaller than that predicted for the $n = 3$ hydrocarbon. This is due, at least in part, to the fact that the Se–C bonds in the salt of **31** are about 0.4 Å longer than the C–C bonds in the 3-21G SCF optimized structure for the $n = 3$ hydrocarbon. The synthesis and X-ray structure determination of the $n = 3$ hydrocarbon are obviously necessary for a meaningful comparison between theory and experiment to be made.

B. Tricyclo[3.3.2.0^{3,7}]dec-3(7)-ene (35)

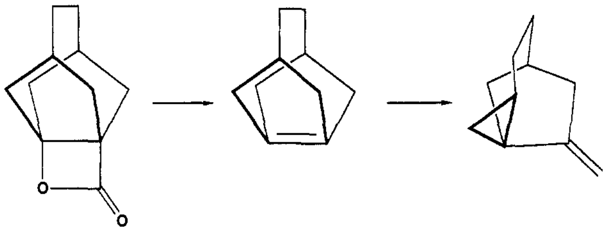
A derivative (**33**) of the $n = 2$ hydrocarbon, in which a benzo rather than an ethano group bridges the bicyclo[3.3.0]oct-1(5)-ene moiety was the first member of this homologous series (**1**) to be prepared.[69] A wide variety of known reaction sequences, which proved successful in the synthesis of unbridged alkene **2**, failed to transform readily available diol **32** into **33**. Finally, it was found that, in refluxing tetraglyme, the (dimethylamino)dioxolane derived from **32** reacted with several different Lewis acids to form **33**.



32 33

Not surprisingly, alkene **33** did not survive the extreme reaction conditions necessary for its formation. In the presence of diphenylisobenzofuran (DPIBF), the Diels–Alder adduct of **33** with DPIBF was isolated. In the absence of DPIBF to trap **33**, the $_{\pi}2_s + _{\pi}2_s$ dimer of **33** was obtained.

The parent $n = 2$ hydrocarbon (**35**) was subsequently prepared by pyrolysis of β-lactone **34**.[70] The large OSE (Table I) of **35** is presumably responsible for the striking stability toward loss of CO_2 that was found for **34**. Nevertheless, pyrolysis of **34** in refluxing tetraglyme in the presence of DPIBF led to the loss of CO_2 and the isolation of the Diels–Alder adduct of **35** with DPIBF. In the absence of DPIBF, the expected $_{\pi}2_s + _{\pi}2_s$ dimer was isolated.



34 35 36

Pyrolysis of **34** in a flow system at temperatures above 450 °C also resulted in the loss of CO_2 and allowed the matrix isolation of **35** by Michl and co-workers.[11] They observed a weak band in the IR spectrum of **35** at 1557 cm^{-1}, which proved to be the strongest band in the Raman spectrum. The assignment of this band as the double-bond stretch was strengthened by a MNDO calculation, which, after scaling (to bring the double bond stretching frequencies calculated by MNDO for ethylene and for tetramethylethylene into agreement with experiment), predicted the double-bond stretch in **35** to occur at 1546 cm^{-1}.

As noted above, the double-bond stretch in both **31** and **35** is IR active. This fact is somewhat surprising, since the stretching of a symmetrically substituted double bond would not be expected to give the change in dipole moment that is required for absorption of IR radiation. The explanation for the IR activity in **35** was provided by Michl and co-workers, who obtained its polarized IR spectrum.

Michl and co-workers found that the double bond stretching vibration is polarized perpendicular, rather than parallel, to the C–C double bond. This finding, which agrees with the polarization predicted for this vibration by MNDO, suggests that the normal mode for "double-bond stretching" in 35 contains a component that changes ϕ at both pyramidalized carbons. This component alters the molecular dipole moment perpendicular to the C–C double bond and, thus, makes the absorption of IR irradiation by 35 allowed.

Michl and co-workers were able to obtain the partially oriented sample of 35 that was necessary for the IR polarization study because the pyramidalized alkene was found to have a broad UV absorption with a maximum around 245 nm. Irradiation of a randomly oriented sample of 35 with the linearly polarized 248-nm radiation from a KrF laser selectively destroyed those molecules whose C–C double bonds were properly oriented for absorption of this radiation.

The decrease in the UV and IR absorption of 35 was accompanied by an increase in the IR absorption of another alkene. This alkene was also formed when 34 was pyrolyzed at very high temperatures or when 34 was passed through a hot tube, under conditions where formation of 35 was known to be 90% complete, and the pyrolysate was then passed through a second, hotter zone.[71] Thus, it appears that 35 is both thermally and photochemically labile and undergoes conversion to the same product upon either pyrolysis or photolysis.

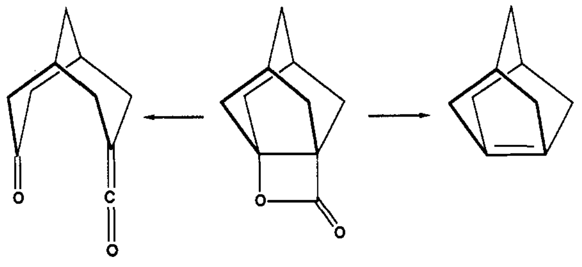
The rearrangement product of 35 was identified as 36.[71] The two structures are related by a vinylcyclopropane rearrangement. However, in contrast to the usual situation, where the cyclopentane derivative is lower in energy than the isomeric vinylcyclopropane, 35 is obviously thermodynamically less stable than 36. This reversal is all the more dramatic, because 36 is an especially strained vinylcyclopropane. It contains a *trans*-bicyclo[5.1.0]octane moiety, whose presence is presumably responsible for its observed lability toward acid-catalyzed rearrangement to 2,6-dimethylenebicyclo[2.2.2]octane. The same product is formed on pyrolysis of 36 at elevated temperatures.

From the fact that 35 rearranges to 36, the difference between the heats of formation of cyclopentene and vinylcyclopropane, and an estimate of the additional strain present in vinylcyclopropane 36, it was possible to set a lower limit of 27 kcal/mol as the amount by which the OSE of 35 exceeds that of cyclopentene.[71] As shown in Table I, both the ab initio and MNDO values for the OSE of 35 exceed this experimentally set minimum value, but the MM2 value does not.[9] In their study of the sesquinorbornenes Houk and co-workers noted that the MM2 potential for pyramidalization of a doubly bonded carbon in a five-membered ring is too soft,[65] and, presumably, this is why the MM2 value for the OSE of 35 is too small.

C. Tricyclo[3.3.1.0^{3,7}]non-3(7)-ene (39)

β-Lactone 38 was prepared as an obvious, potential precursor of the $n = 1$ member (39) of this series of pyramidalized alkenes.[70] However, 38 proved significantly more resistant to loss of CO$_2$ than its $n = 2$ homologue (34). Even after flash vacuum pyrolysis at 550 °C, 50% of 38 was recovered, and the major pyrolysis product at this temperature was not the $n = 1$ alkene (39), but, instead, keto ketene 37.[72]

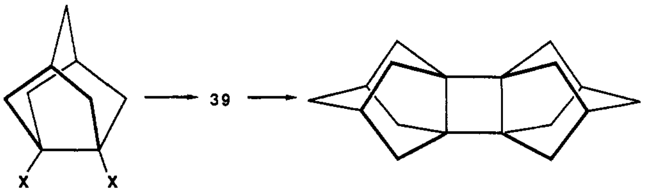
Ordinarily, β-lactones decarboxylate on pyrolysis because formation of alkene plus CO$_2$ is about 40 kcal/mol enthalpically more favorable than formation of carbonyl plus ketene. In the case of 38, decarboxylation should be entropically more favorable, too. The formation of 37 on pyrolysis of 38 at 550 °C was taken to be indicative of the very substantial amount of OSE that must be present in 39.[72]



37 38 39

At still higher pyrolysis temperatures, entropy began to dominate, and CO$_2$ loss was observed. However, although a small amount of the dimer of 39 was formed, the major product obtained was 2,6-dimethylenebicyclo[2.2.1]heptane. Presumably, 39 was formed, but under the conditions necessary for its generation from 38, it too underwent a retrograde vinylcyclopropane rearrangement.[71] Under the pyrolysis conditions, this was apparently followed by a second rearrangement, exactly analogous to that found in 36 at similarly elevated temperatures.

Although the β-lactone route to 39 proved unsuccessful, the $n = 1$ alkene was successfully generated from diodide 41, which was prepared from diol 40.[72]



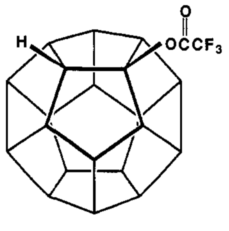
40, X = OH
41, X = I

42

Treatment of 41 with *n*-butyllithium in THF at −78 °C led to the isolation of the expected $_{\pi}2_s + {}_{\pi}2_s$ dimer (42) of 39. In the presence of DPIBF, the Diels–Alder adduct of 39 with DPIBF was isolated.

D. Dodecahedrene (44)

Dodecahedrene (44) also contains a bicyclo[3.3.0]oct-1(5)-ene moiety in which the sense of pyramidalization is the same as that in the homologous series of pyramidalized alkenes 1. Although ab initio calculations have yet to be performed on 44, MM2 calculations predict a value of ϕ = 42.5° and an OSE of 15.5 kcal/mol, and MNDO calculations predict ϕ = 41.7° and an OSE of 42.3 kcal/mol.[73] These values are each somewhat less than the corresponding values for 1, n = 2 (MM2: ϕ = 48.8° and OSE = 18.2 kcal/mol;



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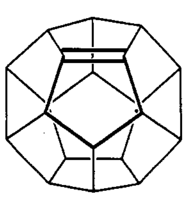


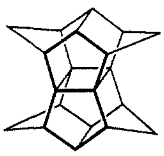
44

MNDO: $\phi = 43.5°$ and OSE = 46.9 kcal/mol).[71] From the similarities of the MM2 and MNDO OSEs computed for 1, $n = 2$ (35), and 44, the ab initio value for the OSE of 44 might be expected to be slightly less than 37 kcal/mol, which is the value for the OSE of 1, $n = 2$, that is obtained from ab initio calculations (Table I).

Marshall, Paquette, and co-workers have obtained indirect evidence for the formation of 44 in a gas-phase reaction performed in an ion cyclotron resonance mass spectrometer.[74] Reaction of (trifluoroacetoxy)dodecahedrane (43) with both hydroxide and methoxide produced trifluoroacetate ion, but reaction with ethoxide did not. These results and the calculated enthalpies of the trifluoroacetate elimination reactions with the same bases to form tetramethylethylene suggest that formation of 44 from 43 releases about 40 kcal/mol less energy.[75] An OSE for 44 of about this size would be consistent with the results of the MNDO calculations.

E. Bissecododecahedrenes (46 and 47)

Despite the fact that MM2 calculations find **46** and **47** each to have somewhat pyramidalized double bonds, these alkenes are both computed to have negative OSEs and thus to be hyperstable.[76a] Prinzbach and co-workers prepared **46** from pagodane (**45**) as a possible intermediate in the synthesis of dodecahedrane.[77] Direct conversion of **45** to **46** proved thermodynamically unfavorable.[76b] However, addition of bromine across one of the bonds of the cyclobutane ring in **45**, followed by reduction with zinc, afforded **46**.[76a]



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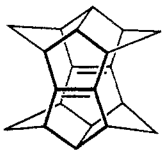

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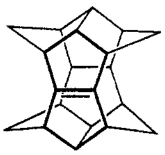


47

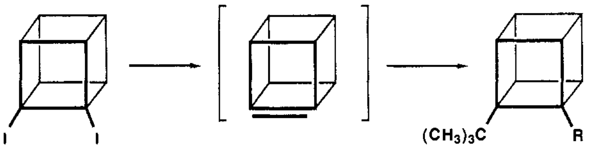
Prinzbach and co-workers reported both PE and UV spectroscopic evidence for strong through-space interaction between the double bonds in **46**.[76a] They also found that, upon one-electron oxidation, both **45** and **46** give the same, delocalized, radical cation.[76c] In accord with the greater hyperstability predicted for monoene **47**, diene **46** proved more reactive toward a variety of double-bond addition reactions.[76a]

VI. Cubene (9) and Homocub-4(5)-ene (53)

Cubene (**9**) may be viewed as a derivative of bicyclo[2.2.0]hex-1(4)-ene (**7**) in which a rigid polycyclic skeleton enforces substantial pyramidalization of the doubly bonded carbons. In fact, as shown in Table I, the pyramidalization angle in **9** is computed to approach 90°. Nevertheless, as discussed in section II.B, because of the ease of pyramidalizing the doubly bonded carbons in **7**, the OSE computed for **9** exceeds that of **7** by <50%.

For the same reason, despite the fact that the value of ϕ computed for cubene is substantially greater than that computed for the $n = 1$ member of series **1** (**39**), the OSEs of the two alkenes are calculated to be similar (Table I). This computational finding led Hrovat and Borden to predict[9] that **9** should be preparable by the same reaction used for the synthesis of **39**—reductive elimination from a diiodide precursor.[72] This prediction has been tested and confirmed by Eaton and Maggini.[79a]

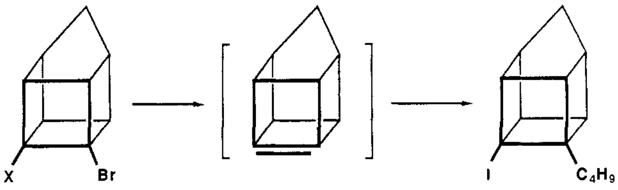
They prepared 1,2-diiodocubane (**48**) and found that on treatment with excess *tert*-butyllithium a mixture of *tert*-butylcubane (**49**) and (2-*tert*-butylcubyl)cubane (**50**) were formed. The structure of the latter compound was established unequivocally by an X-ray crystal structure,[79b] which showed an unusually short (1.46 Å) C–C bond connecting the two cubyl moieties. The formation of **49** presumably occurs by the addition of *tert*-butyllithium to the pyramidalized double bond of cubene (**9**). Reaction of the resulting alkyllithium reagent with another molecule of **9** would result in the formation of **50**. Independent evidence for the formation of **9** was obtained by trapping it as a Diels–Alder adduct.



48 9 49, R = H

50, R = C_8H_7

Since a promising precursor of bromo iodide **51** had already been reported in the literature, Hrovat and Borden sought to verify their own prediction[9] by generating homocub-4(5)-ene (**53**) from **51**.[80] Treatment of **51** with *n*-butyllithium afforded iodide **54**, the product of formal replacement of the bromine in **51** by an *n*-butyl group. That this was not the mechanism by which **54** was formed was indicated by the complete lack of reactivity of dibromide **52** toward *n*-butyllithium. Instead, Hrovat and Borden invoked the addition of *n*-butyllithium to the double bond of **53**, followed by lithium–iodine exchange in the *tert*-alkyllithium thus generated, in order to rationalize the formation of **54**. Subsequently, Schafer and Szeimies published their finding that use of *tert*-butyllithium leads to formation of *tert*-butylhomocubane.[81] Direct evidence for the intermediacy of **53** in these reactions was obtained by Diels–Alder trapping of it.[80]



51, X = I

52, X = Br

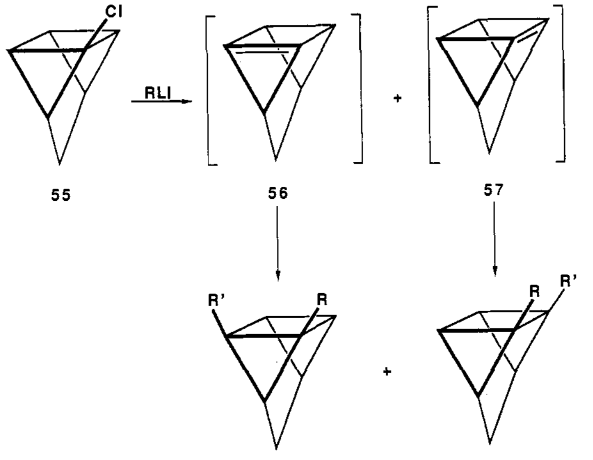
53

54

VII. Quadricycl-1(7)-ene (56)

Quadricycl-1(7)-ene may be viewed as a derivative of bicyclo[2.1.0]pent-1(4)-ene (**4**). Therefore, as discussed in section II.B, the enforced pyramidalization of the double bond in **56** probably should not result in a substantially greater OSE than that present in **4**. Szeimies and co-workers have succeeded in generating a mixture of **56** and the isomeric quadricycl-1(5)-ene (**57**) by treatment of 1-chloroquadricyclane (**55**) with strong bases.[3a,82]

The product isolated after reaction of **55** with *n*-butyllithium was **58**, the formal product of replacement of the chlorine in **55** by *n*-butyl. That this product was



58, R = C_4H_9, R' = H

59, R = C_4H_9, R' = CH_3 60, R = C_4H_9, R' = CH_3

61, R = C_4H_9, R' = D   62, R = C_4H_9, R' = D

63, R = $N(CH_3)_2$, R' = H

64, R = SC_2H_5, R' = H

actually formed by addition of *n*-butyllithium to the pyramidalized double bonds in a mixture of **56** and **57** was indicated by quenching the reaction mixture with bromomethane[82a] or with D_2O.[82b] Mixtures of, respectively, **59** and **60** and **61** and **62** were obtained, in which the 1,7-disubstituted quadricyclane predominated. These experiments show that **56** is the kinetically favored elimination product from **55** and that none of the torsionally strained quadricycl-1(2)-ene is formed.

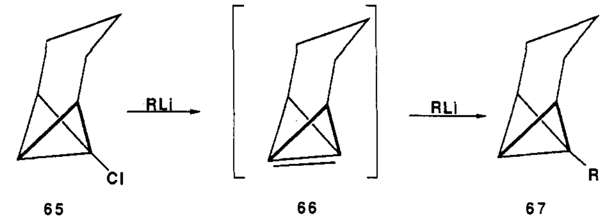
Szeimies and co-workers obtained several additional pieces of evidence for the formation of **56** (and **57**) from **55**. For example, treatment of optically active **56** with lithium dimethylamide gave **63** that was 96% racemic.[82b] In the absence of strong base, **56** failed to react with lithium ethanethiolate, but in the presence of nonnucleophilic lithium amide bases, thioether **64** was isolated. Finally, in the presence of anthracene, the expected Diels–Alder adduct of **56** (but not **57**) was isolated.

VIII. Tricyclo[n.1.0.0$^{2,n+3}$]alk-1(n + 3)-enes

This series of molecules may be viewed as 2,4-bridged derivatives of bicyclo[1.1.0]but-1(3)-ene (**3**). Since, as first noted by Szeimies[83a] and discussed in section II.B, **3** is predicted to contain a pyramidalized double bond, bridging is again not expected to increase substantially the OSE. This prediction has been tested computationally.[9] As shown by the results contained in Table I, the OSE of the $n = 3$ member (**8**) of this series is computed to be only 8.1 kcal/mol (14%) greater than that of **3**. Both the $n = 4$ (**66**) and $n = 3$ (**8**) members of this series have been prepared by Szeimies and co-workers.[3a]

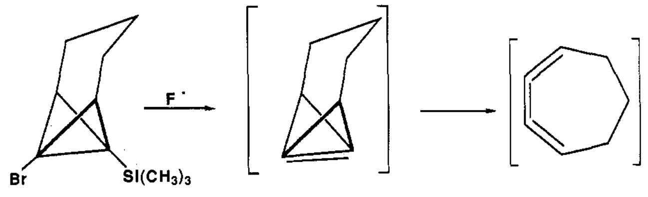
A. Tricyclo[4.1.0.0^{2,7}]hept-1(7)-ene (66)

When chloride **65** was allowed to react with excess alkyllithium, substitution products **67** were formed.[83a] Several lines of evidence were presented in favor of the intermediacy of **66**, the most convincing of which was incorporation of deuterium into **67** when the reaction was quenched with D_2O. Other nucleophiles have been found to add to the pyramidalized double bond of **66**.[3a,83b,c]



When nonnucleophilic bases were employed and dienes were included in the reaction mixture, Diels–Alder adducts of **66** were isolated.[84a–d] Szeimies and co-workers have explored some of the chemistry of the adducts,[84a,b] which may be viewed as derivatives of either [4.1.1]- or [3.1.1]propellane, depending on the diene used to trap **66**. Competition experiments provided evidence for the intermediacy of free **66** in the Diels–Alder trapping reactions.[84d]

Szeimies and co-workers found that **66** could also be generated by an elimination reaction involving fluoride-induced desilylation of **68** in DMSO at 55 °C.[85]



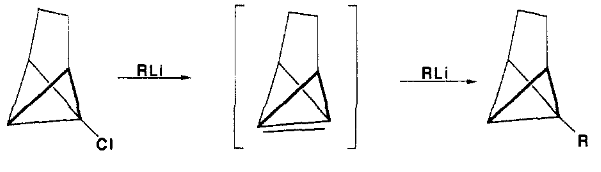
The pyramidalized alkene was trapped as a Diels–Alder adduct with DPIBF and with anthracene. However, in contrast to the base-catalyzed elimination reactions from **65** at −20 °C, the Diels–Alder adduct of 1,2,3-cycloheptatriene (**69**) was also isolated.

The adduct of **69** was the minor product when DPIBF was used as the trapping agent but the major product when anthracene was employed. The ratio of Diels–Alder adducts of **66** and **69** was found also to depend on the concentration of the trapping agent and on the reaction temperature, with lower concentrations of trapping agent and higher reaction temperatures favoring formation of the Diels–Alder adduct of **69**. The latter result explains why adducts of **69** were not isolated from the base-catalyzed elimination reactions from **65** at low temperatures. Szeimies and co-workers interpreted these results in terms of a rearrangement of **66** to **69**. Less efficient trapping of **66** and higher temperatures would both be expected to favor its rearrangement.

Although calculations on **66** have not been reported, calculations on both the lower homologue (**8**)[86] and on unbridged bicyclo[1.1.0]but-1(3)-ene (**3**)[16] found a vibration of low frequency, which was, in fact, imaginary at some levels of theory. The low-frequency vibration was of b_1 symmetry and involved ring deformation. The predicted existence of a low-frequency ring deformation mode in these molecules is consistent with the finding that **66** undergoes ring opening to **69** at quite modest temperatures.

B. Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene (8)

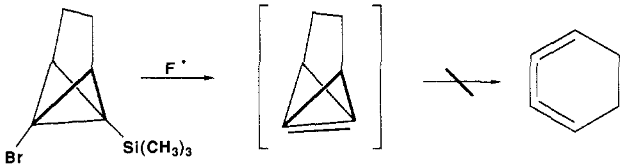
This lower homologue of **66** was, like **66**, first generated by a base-catalyzed elimination reaction.[87] Treatment of chloride **70** with an excess of various alkyllithium reagents gave in each case the product (**71**)



70 8 71

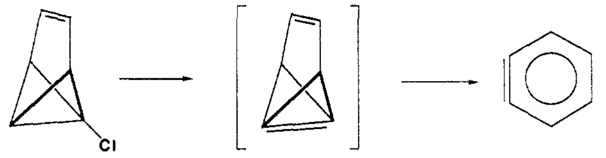
of alkyllithium addition to the double bond of **8**. Evidence for the intermediacy of **8** was obtained by trapping this alkene as the Diels–Alder adduct with anthracene and with DPIBF.

When **8** was generated by fluorodesilylation of **72**, even at temperatures up to 150 °C, no evidence was obtained for rearrangement of **8** to 1,2,3-cyclohexatriene (**73**).[87b] Since **8** is presumably more strained than its higher homologue **66**, the failure of **8** to undergo a rearrangement analogous to that of **66** is, at first, surprising. However, given the fact that **8** is computed to have an OSE of only about 8 kcal/mol more than the unbridged alkene (**3**), it is highly unlikely that **8** is significantly more strained than **66**. In contrast, 1,2,3-cyclohexatriene (**73**) is undoubtedly considerably more strained than 1,2,3-cycloheptatriene (**69**), and this provides a reasonable rationalization for why **8** does not rearrange to **73** under conditions where **66** rearranges to **69**.



72 8 73

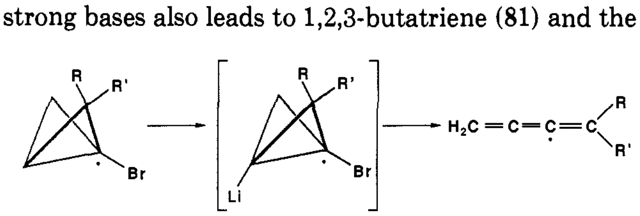
When an additional double bond was introduced into the skeleton of **8**, only a rearrangement product could be intercepted.[88] Thus, reaction of 1-chlorobenzvalene (**74**) with excess *n*-butyllithium at −105 °C yielded only *n*-butylbenzene, presumably formed by addition of *n*-butyllithium to the benzyne (**76**) rearrangement product of dehydrobenzvalene (**75**). Benzyne could be trapped as a Diels–Alder adduct, and in competition experiments benzyne, generated independently, exhibited the same Diels–Alder reactivity as that observed when **74** was treated with strong base.



74 75 76

Generation of the benzo derivative of **75** similarly afforded only products formed from 2,3-didehydronaphthalene. Obviously, the introduction of unsaturation into the two-carbon bridge in **8** greatly enhances the propensity for rearrangement to occur. Since it seems unlikely that the additional double bond significantly increases the strain energy of **8**, it seems probable that the aromatic π system that is present in the rearrangement product provides a driving force that favors rearrangement, both thermodynamically and kinetically.

It should be noted that treatment of 1-bromobicyclo[1.1.0]butane (**77**) and alkyl derivatives with strong bases also leads to 1,2,3-butatriene (**81**) and the alkyl derivatives thereof that would be expected to be formed by base-catalyzed elimination to generate **3**, followed by rearrangement.[89] However, a ^{12}C label at C-1 of **78** was found to appear only at C-3 of **82**, instead of distributed nearly equally between C-2 and C-3 as required by the intermediacy of **3** in this reaction. Since **3** is apparently not involved in the observed rearrangement, the authors suggested that **80** might be the species that underwent the highly regioselective rearrangement that is required by the results of the labeling study.

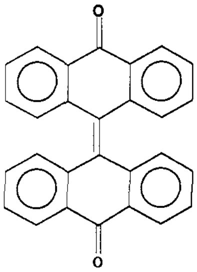


77, R = R' = H
78, R = R' = CH$_3$
79, R = R' = H
80, R = R' = CH$_3$
81, R = R' = H
82, R = R' = CH$_3$

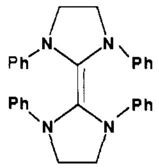
IX. Anti-Pyramidalized Alkenes

Although much remains to be learned about syn-pyramidalized alkenes, the amount of data in the first eight sections of this review shows that quite a bit of effort has already gone into their study. In contrast, practically nothing is known about alkenes that are significantly pyramidalized in an anti fashion, despite the fact that, as discussed in section II, antipyramidalization is calculated to be energetically less costly.[6]

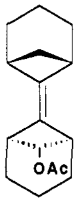
Antipyramidalization provides an alternative to twisting about the C–C double bond for relief of strain in sterically congested ethylenes.[90] For example, the X-ray crystal structures of **83**[91] and **84**[92] find both of them to be pyramidalized in an anti fashion. The pyramidalization angle, ϕ, is 16° in the former molecule and 13° in the latter.



83



84

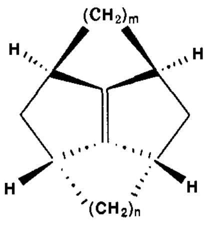


85

The X-ray structure of the less sterically congested **85** gives pyramidalization angles of ϕ = 6–7°.[83c] It should be noted that, even ignoring the acetoxyl group, **85** can have at most C_{2h} symmetry. Since the symmetry plane in **85** does not contain the bonds to the olefinic carbon atoms, a planar geometry at these two atoms is not a stationary point. Therefore, there is essentially zero probability of the geometry at these two atoms being exactly planar.

In order to observe substantial amounts of anti pyramidalization at two doubly bonded carbons, it is likely that the rigid constraints of a polycyclic system will have to be employed. For example, it should be possible to force anti pyramidalization of the doubly bonded carbons in bicyclo[3.3.0]oct-1(5)-ene (**2**) by spanning C-2 and C-8 with a cis-fused chain of methylene groups and C-4 and C-6 with a second chain, also cis-fused, but anti to the first chain.

With a pair of ethano bridges in the resulting tetracyclic alkene (**86**, $m = n = 2$), the pyramidalization angle and the OSE are computed to be, respectively, $\phi = 34.4°$ and OSE = 32.7 kcal/mol with MNDO.[73] The OSE is calculated for anti addition of hydrogen to the double bond in **86** and in **2**. If the ethano bridges in **86**, $m = n = 2$, were syn rather than anti, the resulting syn-pyramidalized alkene would have the same local structure around the double bond as dodecahedrene (**44**), but it would not be as rigid as **44**. MNDO calculations find $\phi = 38.4°$ for the syn isomer of **86**, $m = n = 2$, and an OSE of 35.5 kcal/mol. These values are slightly less than the corresponding numbers computed for **44**.



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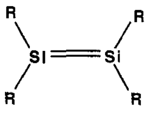
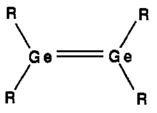
X. *Pyramidalization at Other Doubly Bonded Atoms of Group IV (14)*

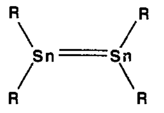
The properties of molecules containing double bonds between elements heavier than carbon in group IV (14) of the periodic table have been reviewed by Cowley and Norman.[93] The anti-pyramidalized equilibrium geometry that is computed for disilene (**87**)[94a] has been attributed to the pyramidal geometries that are preferred by silyl radicals.[95a] It has been shown[95b,96a] that silyl radical pyramidalization further reduces the strengths of the already weak π bonds formed by planar silicon.[97]



87, R = H
88, R = 2,4,6-$(CH_3)_3Ph$
89, R = $[(CH_3)_3Si]_2CH$



90, R = H
91, R = CH_3
92, R = 2,6-$(C_2H_5)_2Ph$
93, R = $[(CH_3)_3Si]_2CH$



94, R = H
95, R = $[(CH_3)_3Si]_2CH$

The most recent calculations predict a value of ϕ of about 35° in **87**.[96] Nevertheless, sterically shielded derivatives of **87** show either no pyramidalization at silicon or substantially less than that computed for the parent molecule.[93,94] For example, the X-ray structure of **88**, the only derivative of **87** yet found to show pyramidalization at silicon, finds $\phi = 18°$.[98] The X-ray structure of **89** should prove interesting, since its ^1H NMR spectrum has been obtained and is consistent with an anti-pyramidalized equilibrium geometry.[99]

The potential surface for silicon pyramidalization in **87** is computed to be quite flat.[94a] The most recent calculations give a barrier to planarity of only about 2 kcal/mol.[96] It has been suggested, therefore, that steric repulsion between bulky substituents at silicon could easily inhibit silicon pyramidalization in derivatives of **87**.[96a] This could account for the lack of pyramidalization observed[93,94] in some of the derivatives for which structural data are available.

A somewhat larger pyramidalization angle and barrier to planarity have been calculated for digermene (**90**) than for disilene (**87**).[100,101] CI calculations on **90** give $\phi = 40°$ and a barrier of 3.6 kcal/mol.[100a] The IR and Raman spectra observed for tetramethyldigermene (**91**) were better fit with an anti-pyramidalized than with a planar equilibrium geometry.[102] Two derivatives of **90** have been studied by X-ray crystallography. The pyramidalization angles found were $\phi = 15°$ for **92**,[103] which, like **88**,[98] is also slightly twisted, and $\phi = 32°$ for **93**.[101,104]

Ab initio SCF calculations, which yielded $\phi = 40°$ and a barrier to planarity of about 3 kcal/mol for digermene (**90**),[100b] gave an anti-pyramidalized equilibrium geometry for distannene (**94**) with $\phi = 46°$ and twice as large a barrier to planarity.[101,105a] MNDO semiempirical calculations predict a similar geometry and barrier height for **94**.[105b] Charge iterative, relativistic, extended-Hückel calculations also predict greater pyramidalization and a larger barrier to planarity on moving down the periodic table from **90** to **94**.[105c]

An anti-pyramidalized equilibrium geometry with $\phi = 41°$ has been found experimentally in the X-ray structure of sterically shielded distannene **95**.[101,106] The fact that distannene **94** is considerably more pyramidalized than digermene **93**, which has the same substituents, provides experimental support for the theoretically predicted trend toward greater anti pyramidalization in doubly bonded atoms of group IV (14) on moving down the periodic table.

The theoretical and experimental data on molecules containing Si–Si, Ge–Ge, and Sn–Sn double bonds put into perspective the material in sections I–IX on alkenes containing pyramidalized C–C double bonds. Unlike the case in alkenes, where substantial pyramidalization of the doubly bonded carbons is the exception, pyramidalization of other doubly bonded atoms of group IV (14) is likely to be the rule. Since substantially pyramidalized geometries at doubly bonded atoms of group IV (14) are exceptional only for carbon, the study of alkenes in which the doubly bonded carbons are pyramidalized is of special interest.

XI. *Conclusions*

In the 20 years since Weinshenker and Greene published the synthesis of **12**,[5] many more pyramidalized alkenes have been prepared. Matrix isolation techniques have allowed spectroscopic data to be obtained on some of these alkenes (e.g., **35**)[11] that are too reactive to be studied under other conditions. It is to be hoped that improved synthetic methods for the generation of pyramidalized alkenes will, in the future, allow the matrix isolation of some of the other highly pyramidalized alkenes discussed in this review. The passage into common usage by organic chemists of techniques like matrix isolation spectroscopy will undoubtedly continue to further the experimental study of pyramidalized alkenes.

It is the strong (and, admittedly, biased) belief of the author of this review that ab inito calculations, which were at one time almost exclusively the province of physical chemists, have already made several significant contributions to this field. These contributions, discussed in section II, have provided not only explanations but also predictions, which have served to stimulate experiments. As has been the case in recent investigations of other types of reactive organic molecules, the synergistic interaction between ab initio calculations and experimental investigations will almost surely continue to advance the study of pyramidalized alkenes in the future.

Acknowledgments. The experimental research on pyramidalized alkenes in the author's group was performed by a talented group of co-workers. Of these Drs. Robert Greenhouse, George Renzoni, Tyze-Kuan (Tim) Yin, Fumio Miyake, and Dave Hrovat deserve special recognition. Dave Hrovat also was responsible for performing many of the calculations discussed in this review and for making all the drawings. Fruitful collaborations with Professors Ernest Davidson, Jon Clardy, and Josef Michl are gratefully acknowledged. Support for the author's research on pyramidalized alkenes was provided by the National Science Foundation. Many of the calculations discussed here were performed at the San Diego Supercomputer Center.

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