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The generation and fate of strained, unsaturated, bicyclic hydrocarbons

Nathan L. Anderson
Iowa State University

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Anderson, Nathan L., Ph.D.

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U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

The generation and fate of strained, unsaturated, bicyclic hydrocarbons

by

Nathan L. Anderson

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GENERAL INTRODUCTION

Format explanation

Two separate studies in bicyclic hydrocarbon rearrangements will be included in this dissertation. Each paper has its own literature review, discussion, and references and is, in that respect, a complete and separate entity. A general summary and references for the introduction follow the second paper.

Subject matter

The first paper in this dissertation is a study of the gas-phase generation of bicyclo[2.2.2]oct-1-ene **1**[1] and the structural determination of its dimers. The literature review gives a historical perspective of Bredt olefins[2] in general and studies of the [2.2.2] system **1** in particular. Additionally, approaches to generating bicyclo[2.2.2]octa-1,2-diene, a "Bredt allene" are discussed.

The second paper is a study of the reactions of bicyclic vinylidenes. The literature review is a survey of vinylidenes and their reactions.[3] Ring contraction and ring expansion reactions[4] are discussed in terms of ring strain. Synthetic approaches to alternative vinylidene precursors are discussed.

PAPER I. THE GAS-PHASE GENERATION AND DIMERIZATION OF BICYCLO[2.2.2]OCT-1-ENE

LITERATURE REVIEW

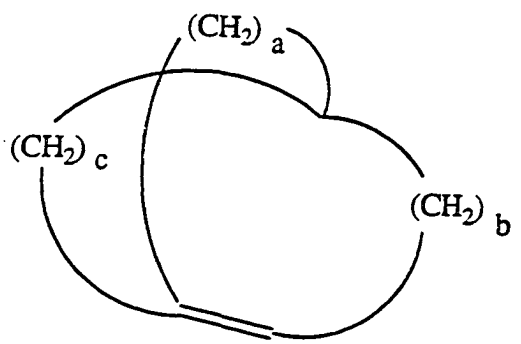
Since Bredt's studies of the dehydrobromination of constrained hydrocarbons in the first quarter of this century[1] and his recognition of the importance of geometric deformation necessary for a double bond to exist at the bridgehead of systems such as camphane and pinane, the study of bridgehead olefins has received special attention. In recognition of the importance of Bredt's work, olefins terminating at the bridgehead of a strained bicyclic system have come to be known as Bredt (or anti-Bredt) olefins and the general rule forbidding such olefins to be known as Bredt's rule.

A typical statement of Bredt's rule is: "On the basis of our conceptions of the positions of atoms in space, in the systems of the camphane and pinane series, as well as in similarly constituted compounds, a carbon double bond cannot occur at the bridging positions A and B (above) of the carbon bridge."[2]

Subsequent to the publication of the general rule several studies ensued with the purpose being to more clearly define the limits of "similarly constituted compounds". In his 1950 review Fawcett[2] attempted to establish a

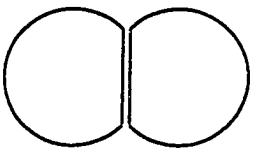
lower limit on the system size in which a bridgehead double bond would be stable.

Fawcett introduced the concept of the *S* number to predict bridgehead olefin stability. The *S* number is the sum of the carbons in the bridges of the bicycle, excluding the olefin carbons and bridgehead carbon ($S = a + b + c$). Although it was eventually proven wrong (vide infra),[3] the suggestions that compounds with $S \geq 7$ should be stable enough to exist as transient

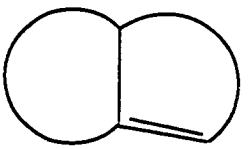


intermediates were important bench marks in the study of Bredt olefins.

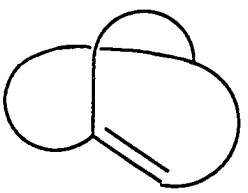
Additionally, Fawcett suggested the exclusion of zero atom bridges from the discussion of Bredt olefins. As pointed out in Warner's later review,[4] there are three major types of bridgehead alkenes; **A**, **B**, and **C**.



Type **A**



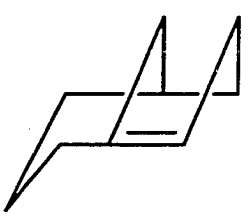
Type **B**



Type **C**

Type **A** olefins are not twisted, except in special cases, and type **B** olefins, with zero-atom bridges, are often excluded and are treated as a special case.

In 1967 two independent syntheses of bicyclo[3.3.1]non-1-ene **1** were reported by Wiseman[3] and by Marshall and Faubl.[5] Both routes afforded



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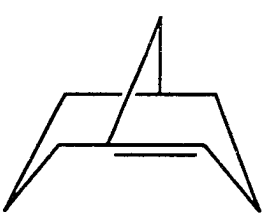
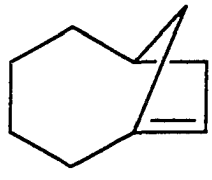


2

isomer **1** rather than **2**. Wiseman suggested that **1** is more stable than **2** because the *trans*-double bond occurs in the eight-membered ring in **1** but in a six-membered ring in **2**, relating the stability of the bicyclic systems to the simpler monocycles.

Wiseman and Pletcher[6] proposed that other Bredt olefins would also display stability and reactivity parallel to that of the corresponding *trans* cycloalkene. Bredt olefins with *trans* cyclooctenes should be the smallest systems to be isolated at room temperature, because *trans* cyclooctene is isolable at room temperature. *trans* Cycloheptene, on the other hand, is only observable at reduced temperature and "certain bicyclic compounds may possibly be isolable with the *trans* double bond in a seven membered ring. Wiseman's stability criterion seems to be the simplest and most generally applicable.

A shortcoming of Wiseman's system is that it fails to predict differences in reactivity of isomeric compounds such as **3** and **4** below. The deformation of



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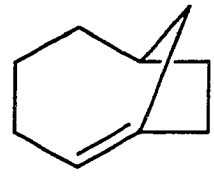
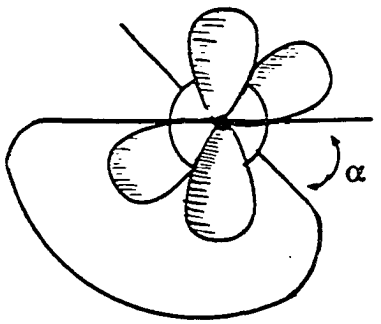


4

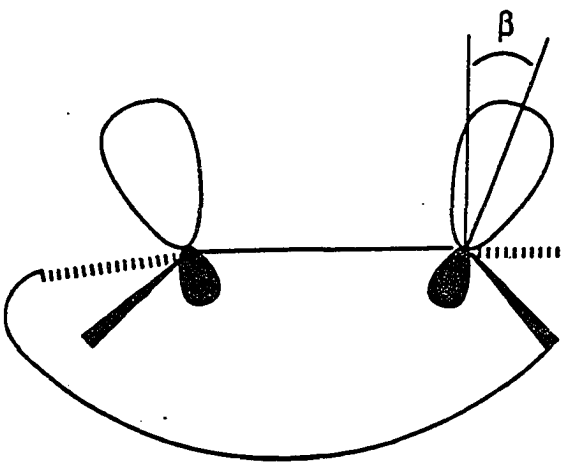
double bonds which leads to instability can be quantitated by force field calculations.[4] This is the approach used by Ermer[7] and by Maier and Schleyer.[8]

Two principle forces are at work in Bredt olefins which contribute to the decrease in bond order and decrease in stability of the double bond.[9] The "pinning back" of the groups substituent to the double bond at once causes: 1) twisting of the π system from planarity (Figure 1.) and 2) out-of-plane bending of the sp^2 centers (Figure 2.). These deformations are accompanied by



α = degree of twist of olefin

Figure 1. Olefin twist



β = degree of bend of olefin

Figure 2. Olefin bend

asymmetric rehybridization of the olefinic carbons. It is suggested[10] that the bridgehead carbon will have greater sp^3 character while the opposite terminus remains relatively sp^2 hybridized (Figure 3.) and, at least in extreme cases, the deformed olefin may be better represented as a dipolar structure rather than a diradical.[10]

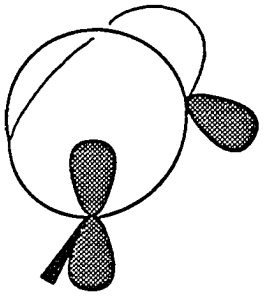


Figure 3. Olefin rehybridization

Ermer's calculations[11] give an interesting view of the separate contributions (twisting and bending) to the overall destabilization of a variety of Bredt olefins. The sum of the twisting V_α and bending V_β is an indicator of the reactivity of the Bredt olefin, non-planar deformation energy V_{oop}. If $V_{oop} \leq 15$ kcal mol^{-1} room temperature stability is suggested and $V_{oop} > 15$ kcal mol^{-1} indicates instability at room temperature.

As an example consider the structure of bicyclo[2.2.2]oct-1-ene **5** predicted by Ermer's calculations (Figure 4.). V_{oop} is calculated to be 35.1 kcal mol^{-1} and V_α and V_β are calculated to be 17.9 kcal mol^{-1} and 17.1 kcal mol^{-1}, respectively. The non-planar deformation energy V_{oop} indicates the degree to which the Bredt olefin resembles an olefin "which has made progress on the reaction coordinate of some reaction leading to saturation of the double bond."

While the separation of twisting and bending doesn't allow better prediction of the overall reactivity or stability of Bredt olefins it does give a clear view of the orbital geometry.

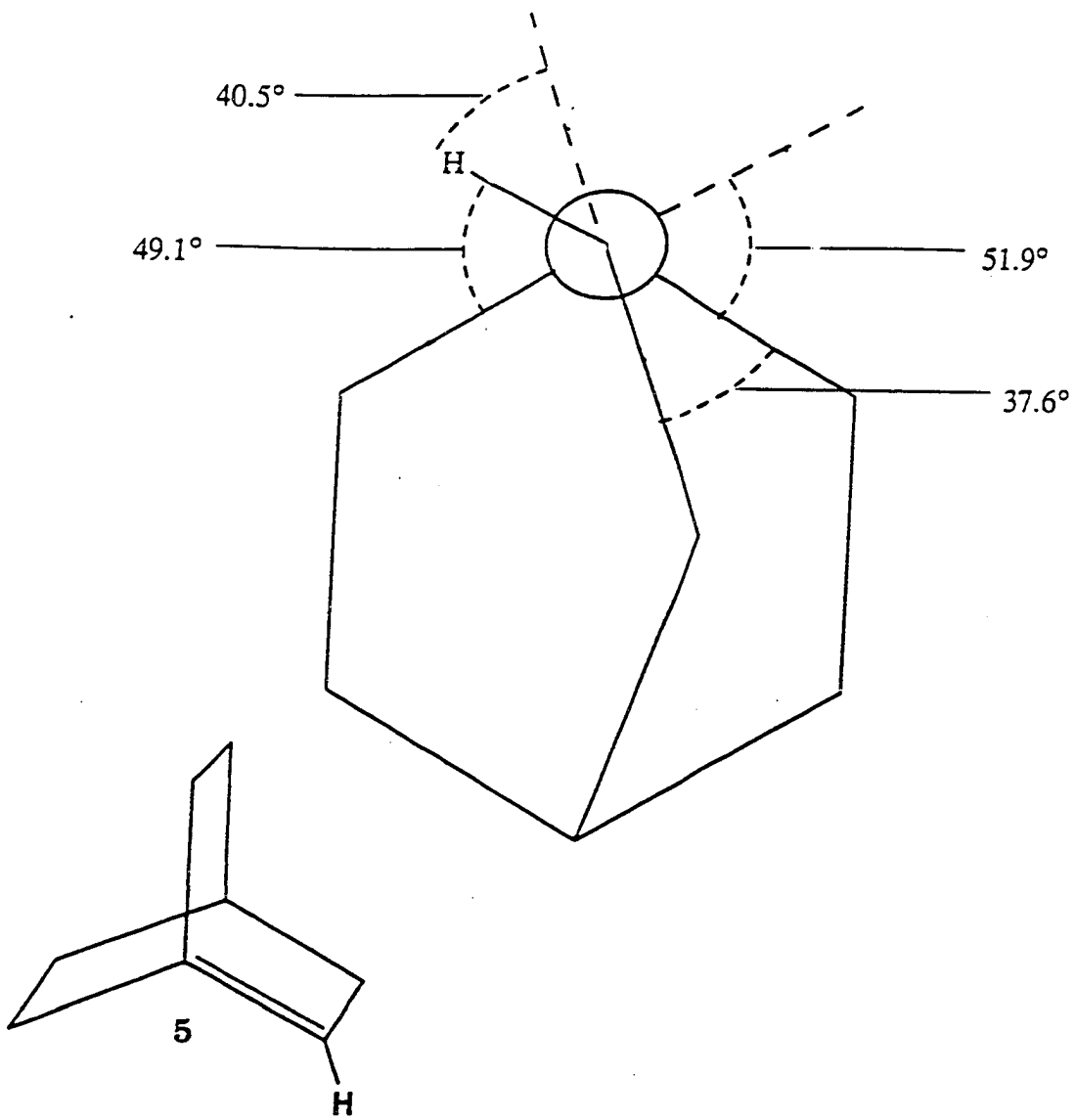


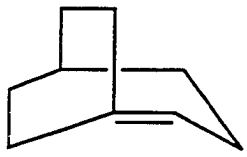
Figure 4. Ermer's structure of bicyclo[2.2.2]oct-1-ene **5**

Burkert[12] and, later, Maier and Schleyer[8] used Allinger's MM1 force field[13] to compare stabilities of Bredt olefins. Burkert reported total strain of the bicycles. Since this method combines strain inherent in the system with strain arising from the twisting and bending of the olefin it is not particularly useful in predicting Bredt olefin stability. Maier and Schleyer, on the other hand, used the olefin strain (OS) approach[9] which separates the skeleton's residual strain from the total strain of the system allowing comparison of the energies associated with the bond deformations.

The strain energy of a Bredt olefin is the sum of the strain of the carbon framework and the extra strain associate with the bent and twisted bridgehead olefin. By substracting the strain energy of the saturated system in its lowest energy conformation from the total energy of the Bredt olefin in its lowest energy conformation OS is determined. OS calculated in this manner relates well to the heat of hydrogenation of the olefin and is, therefore, a good indicator of the reactivity of the olefin.

By comparison of calculated OS with reactivity data Maier and Schleyer developed three categories of Bredt olefin stability: 1) those which can be isolated at room temperature have OS $\leq$ 17 kcal mol^{-1}, 2) those detectable at low temperature have OS between 17 kcal mol^{-1} and 21 kcal mol^{-1}, and 3) Bredt olefins with OS $\geq$ 21 kcal mol^{-1} should be too unstable to be observed except, perhaps, in a matrix.

These calculations are in good agreement with the predictions of Wiseman and the calculations of Ermer. By comparison to Wiseman's work, the Maier and Schleyer calculations have the added benefit of distinguishing



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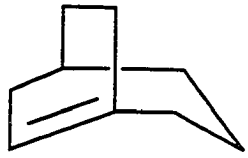


7

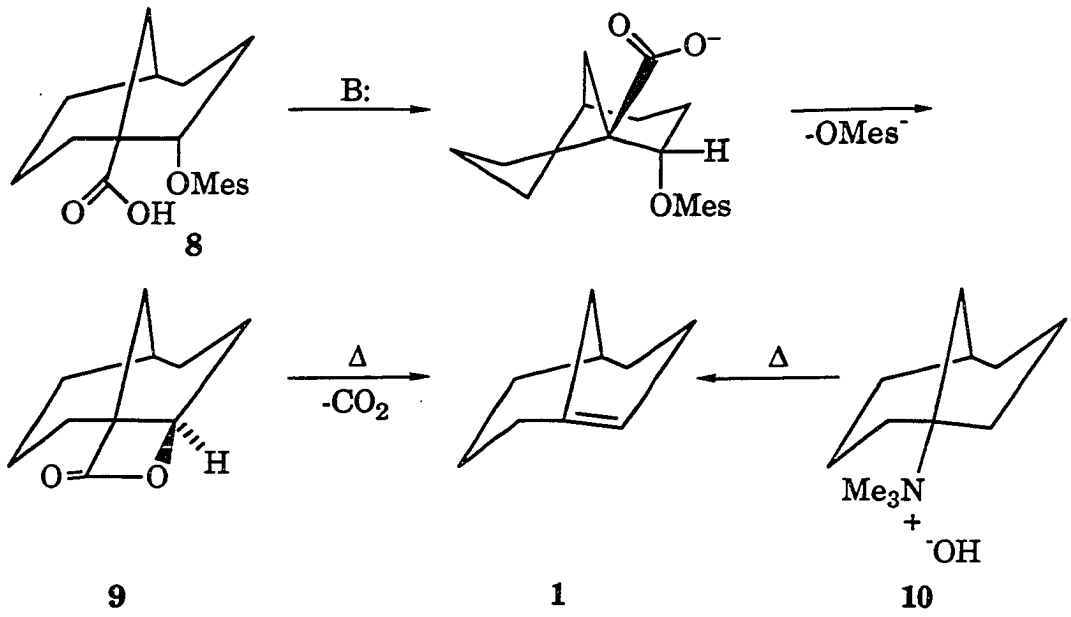
between isomeric Bredt olefins such as the bicyclo[3.2.2]octenes **6** and **7**. OS for **6** and **7** are calculated[9] to be 19.5 kcal mol^{-1} and 20.6 kcal mol^{-1}, respectively. These Bredt olefins are observable at -80 °C[14] and it has been demonstrated that **7** reacts more rapidly than **6**.

Compared to Emer's calculations, the approach of Maier and Schleyer is probably more practical due to the accessibility of MM1. It should be noted that Warner and Peacock[15] have applied MM2 to a series of Bredt olefins for comparison with the MM1 results. The results of the two calculations are not significantly different.

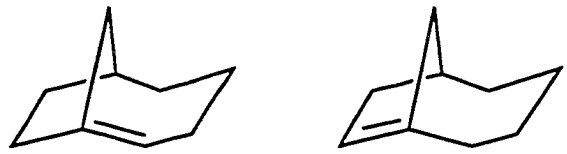
With this as a theoretical perspective of Bredt olefins, let us turn to the experimental reports, beginning with the reports which disproved Fawcett's *S* rule and proceeding to more highly stained systems.

Marshall and Faubl[5] produced the Bredt olefin **1** by base catalyzed decomposition of the mesylate/acid **8** (Scheme 1). Based on the stereochemistry at C-2 of the β-lactone **9**, on the configuration of the olefin **1**, and on analysis of models, it was concluded that the required geometry for elimination must be the twisted boat-boat form of the intermediate.

Wiseman[3] generated the same bicycle *via* thermal, gas-phase decomposition of the quaternary ammonium hydroxide **10**.

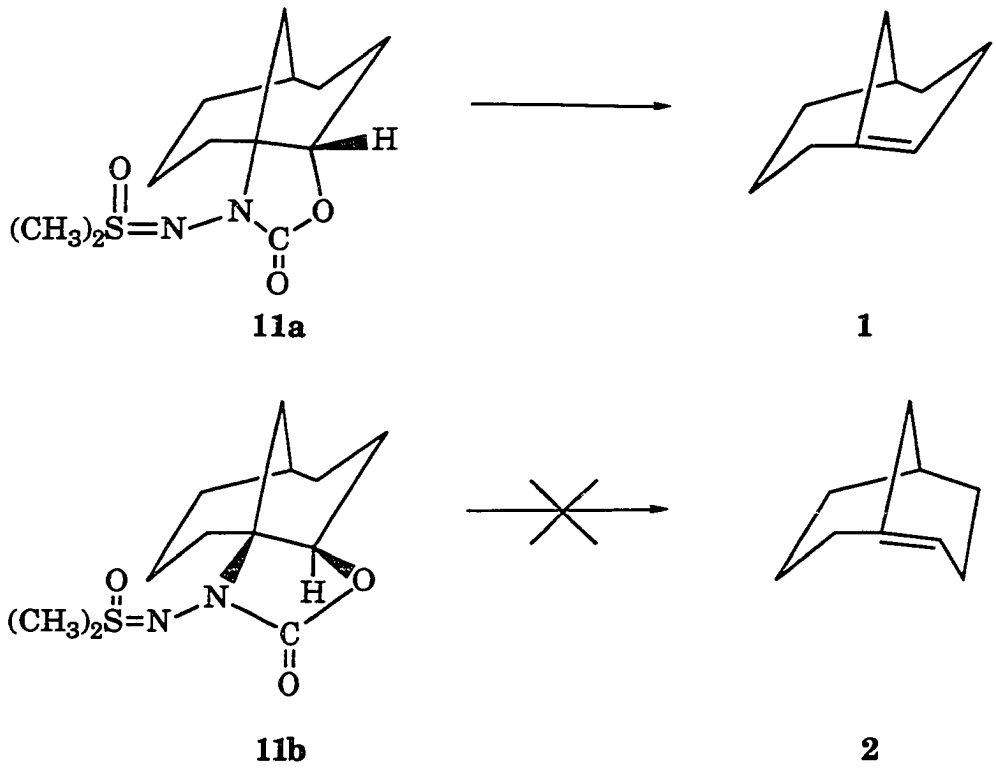


Scheme 1



12 **13**

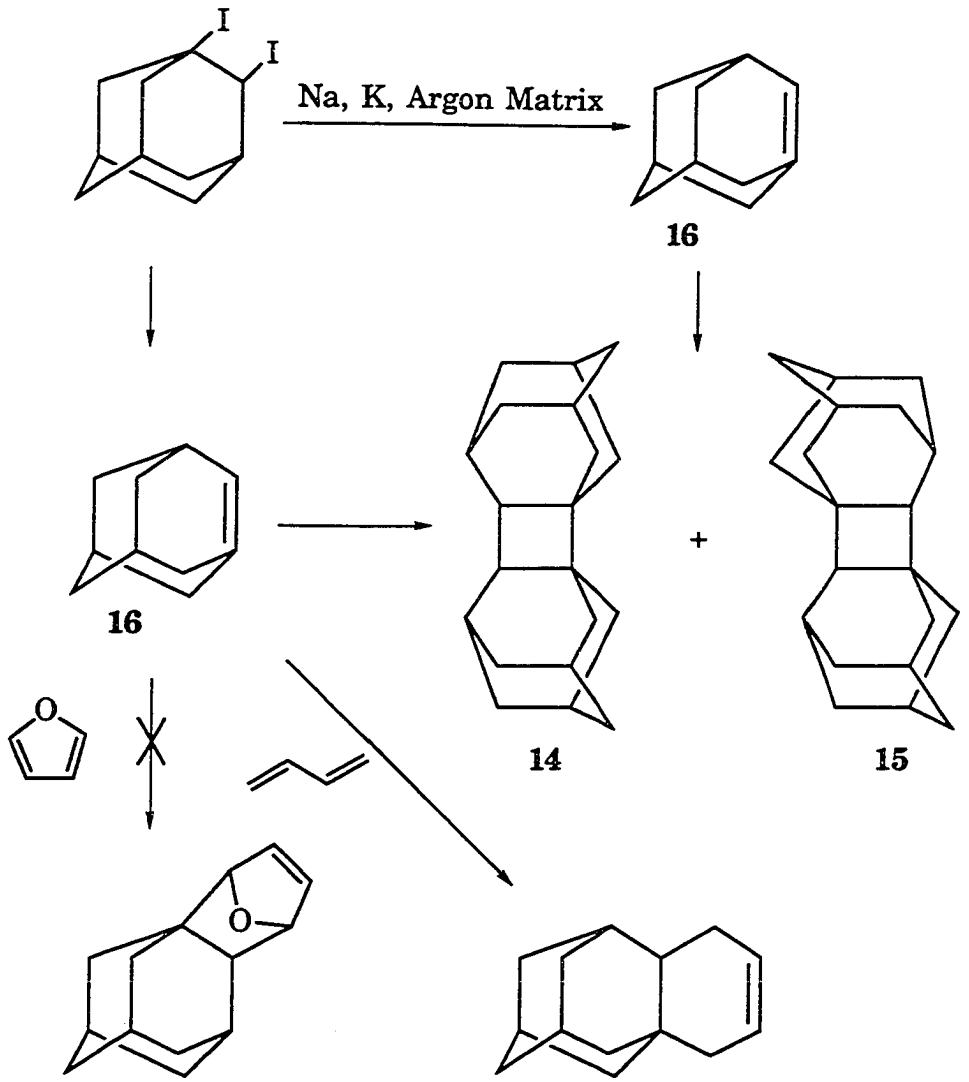
Kim and White[16] produced **1** by thermal decomposition of the exo-sulfonimine **11a** but failed to generate the corresponding isomer of **2** from the endo-epimer **11b** (Scheme 2). The stabilities of other isomers of **1**, bicyclo[4.2.1]non-1-(2)ene **12** and bicyclo[4.2.1]non-1(8)ene **13**, were demonstrated by Wiseman et al.[17]



Scheme 2

While untwisted ethylene units do not tend to dimerize readily, the twist in Bredt olefins gives them a built in predisposition for dimerization. The deformed double bond of a Bredt olefin closely resembles the twisted, pyramidalized transition structure calculated by Segal[18] for the formation of cyclobutane from two ethylenes.

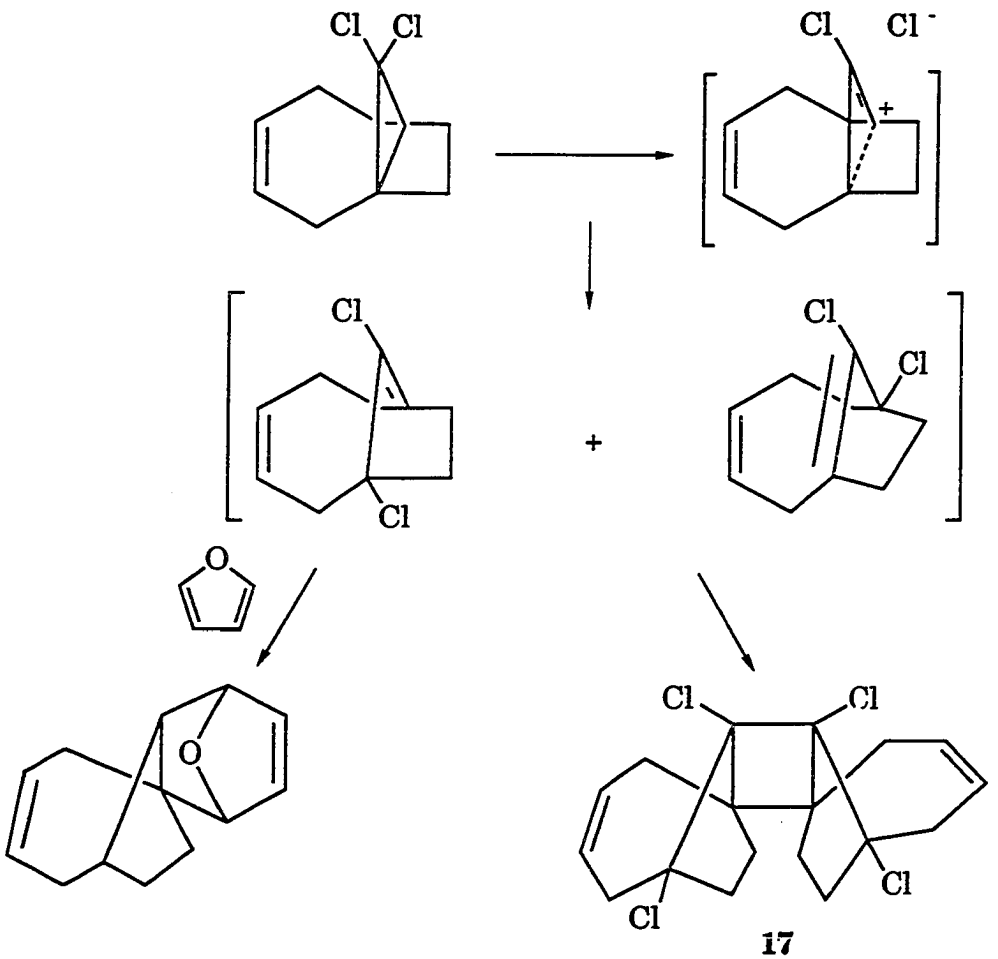
There are several examples of Bredt olefin dimers in the literature, the most published are the head-to-head and head-to-tail adamantene dimers **14**



Scheme 3

and **15**.[19] Attempts to trap the adamantene **16** with furan were unsuccessful, however, it was trapped with butadiene (Scheme 3).[20]

IR and ESR studies[21] of adamantene formed in an argon matrix lend support to the intermediacy of adamantene **16** in the formation of the dimers as



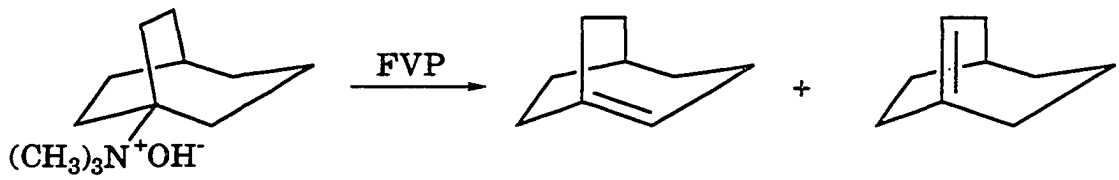
Scheme 4

well as demonstrate that the intermediate is best viewed as an olefin rather than a diradical.

Bredt olefins containing a *trans*-cycloheptene represent the largest system which is proposed to be observable at reduced temperature (below room temperature) but too reactive to be isolated. Several such reactive intermediates have been demonstrated.

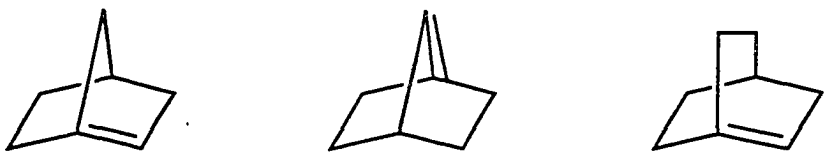
Warner and co-workers[22] reported the crystal structure for the dimer of the 9,9-dichlorotricyclo[4.2.1.$0^{1,6}$]non-3-ene rearrangement product **17** formed neat or in polar solvents. The intermediate Bredt olefin was also trapped with furan (Scheme 4). The head-to-head *R,S* dimer **17** is isolated in ca. 80% yield.

Wiseman and Chong[14] generated the isomeric [3.2.2] Bredt olefins **6** and **7** by pyrolysis of the quaternary ammonium hydroxide **18** (Scheme 5). Two 2 + 2 dimers of the Bredt olefin were inferred by their IR and NMR spectra. The 1:2 ratio of **6**:**7** apparently arises from the statistical advantage of elimination to from **7**. (Force field calculations[8] predict only a 0.9 kcal mol^{-1} difference in energy for the two Bredt olefins.)



18 **6** **7**

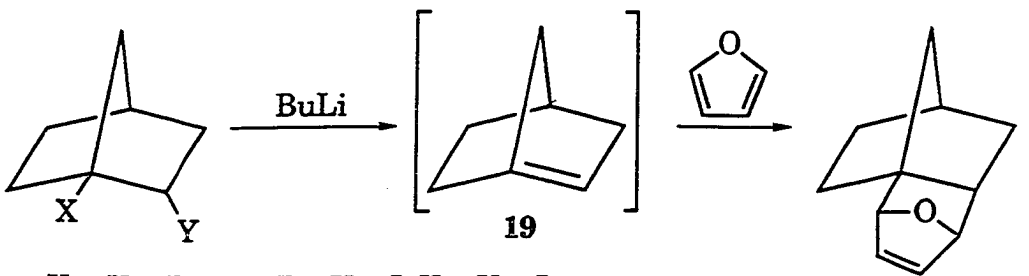
Scheme 5



19 **20** **21**

The *trans*-cyclohexene related bicycles represent the next step in higher energy Bredt olefins. Curiously, the [2.2.1]system **19** & **20** is predicted to be lower in energy than the [2.2.2] system **21** by 5.5 kcal mol^{-1} and 1.9 kcal mol^{-1}, respectively.[8,11]

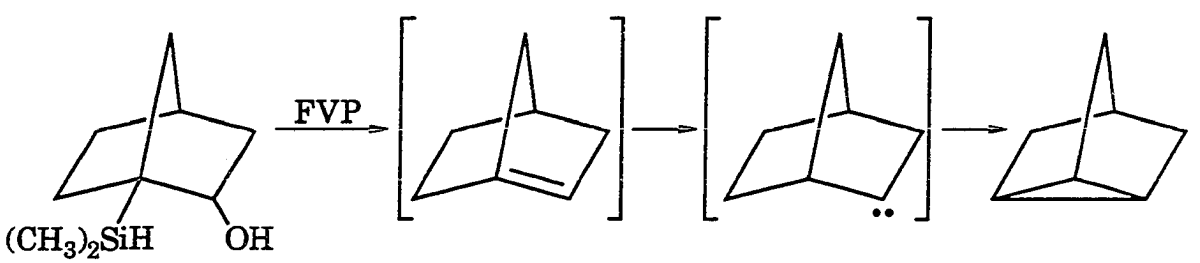
Keese and Krebs[23] demonstrated the intermediacy of **19** by furan trapping of the reductive elimination product of 1,2-dihalonorbornanes (Scheme 6).



X = Y = Br; X = Br, Y = I; X = Y = I

Scheme 6

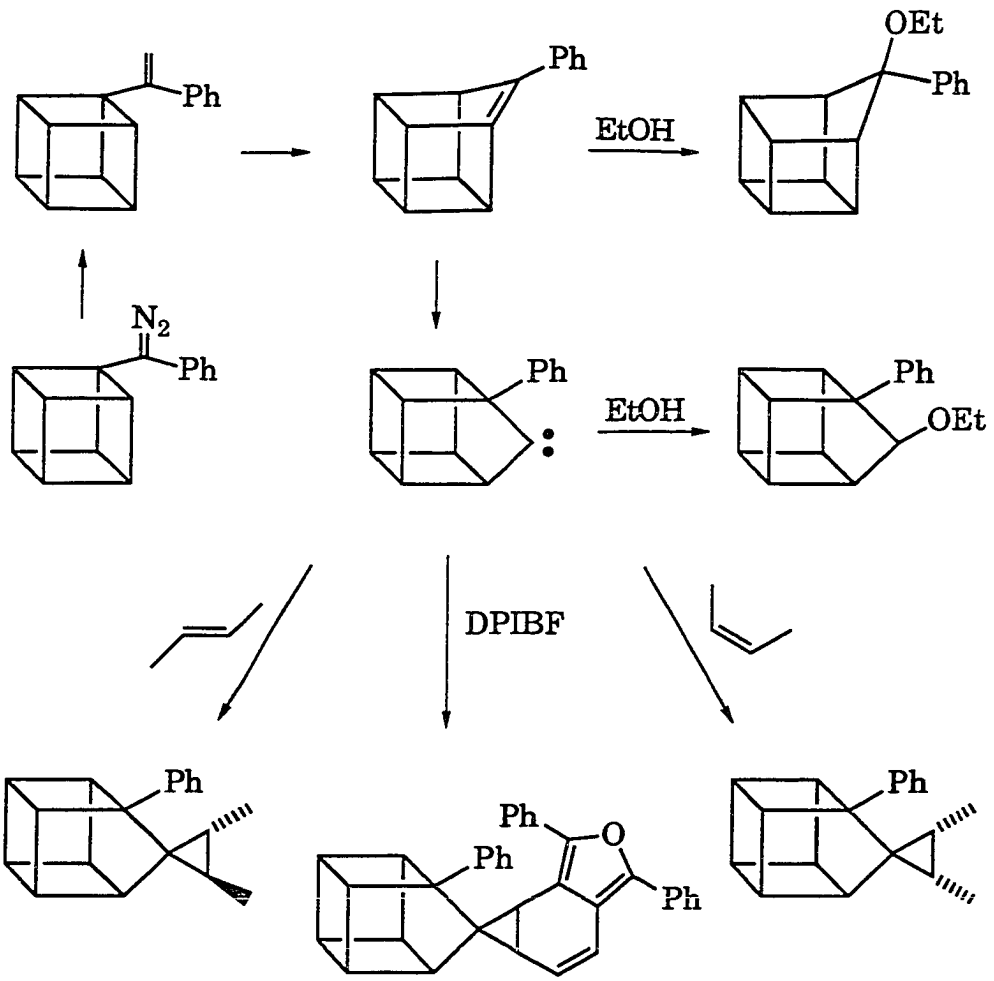
Barton and Yeh[24] have demonstrated the formation of the tricyclene **22** from the pyrolysis of the precursor **23** (Scheme 7). An alkyl shift to form the



Scheme 7

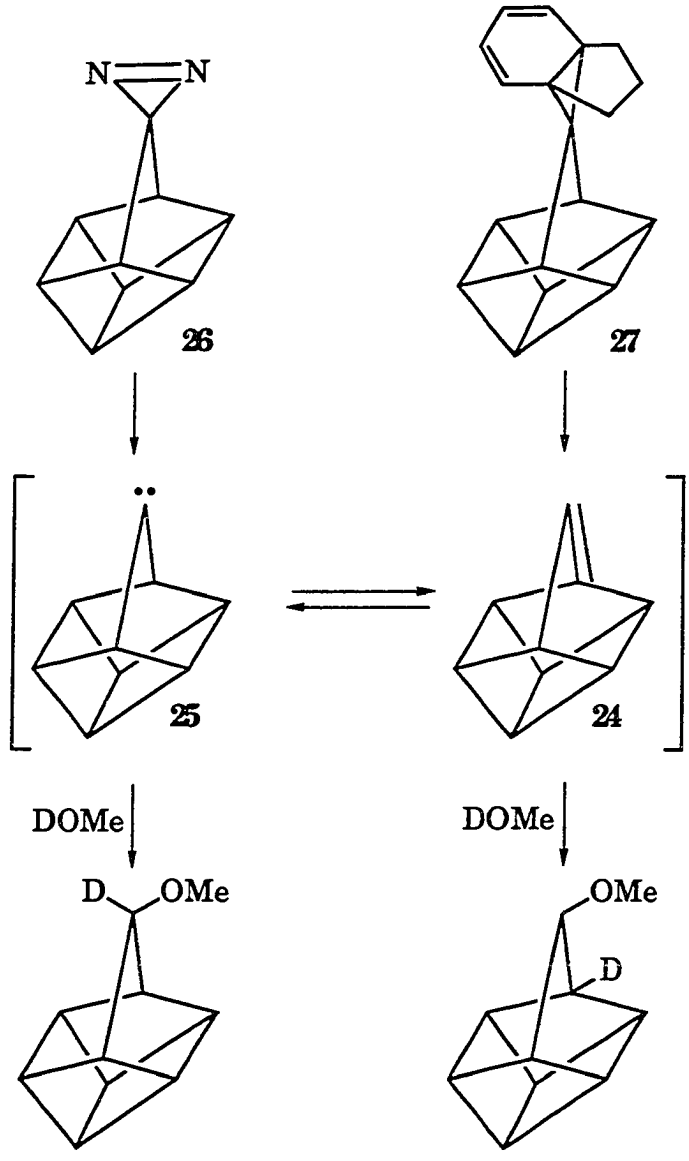
carbene was proposed. Similar chemistry is reported to occur with the 7,7-dimethyl analog of **23** by reaction with iodine at room temperature.

Eaton and Hoffman[25a] have provided another example of such an olefin-carbene interconversion (Scheme 8).



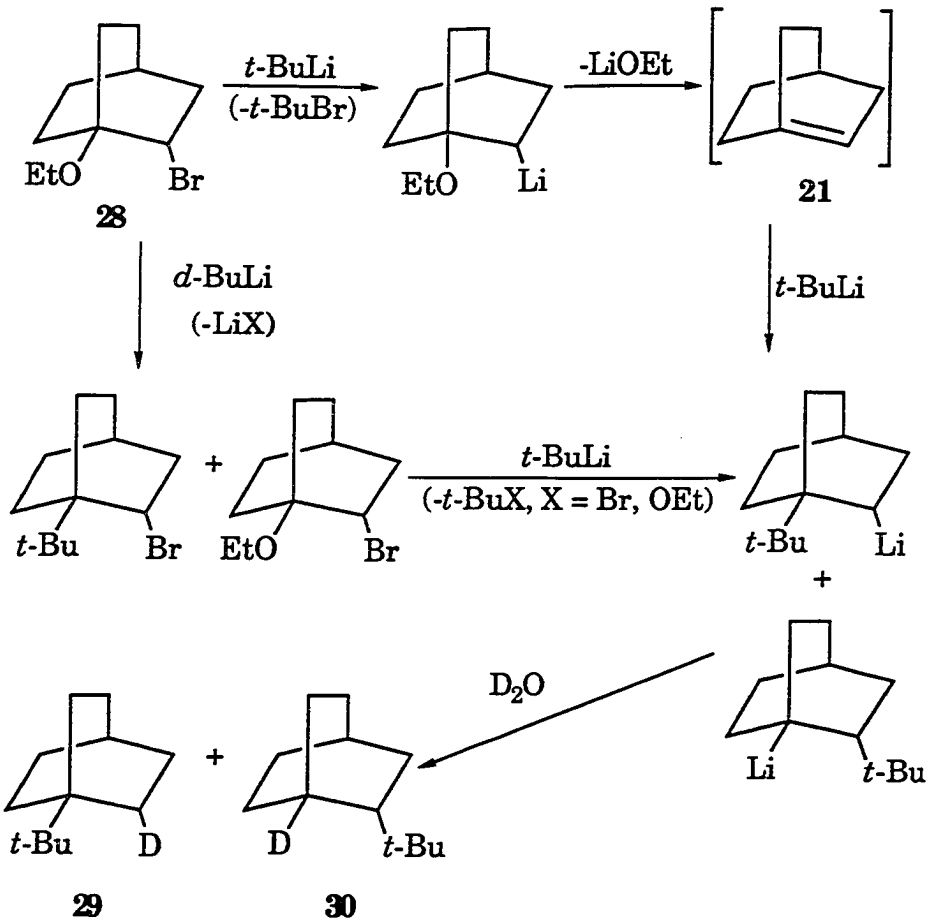
Scheme 8

White and co-workers[25b] have demonstrated the interconversion of 1-homocubene **24** and carbene **25** produced from precursors **26** and **27** (Scheme 9). They have estimated the equilibrium constant to be $0.23 \leq K \leq 4$ by laser flash photolysis and methanol and pyridine quenching experiments.



Scheme 9

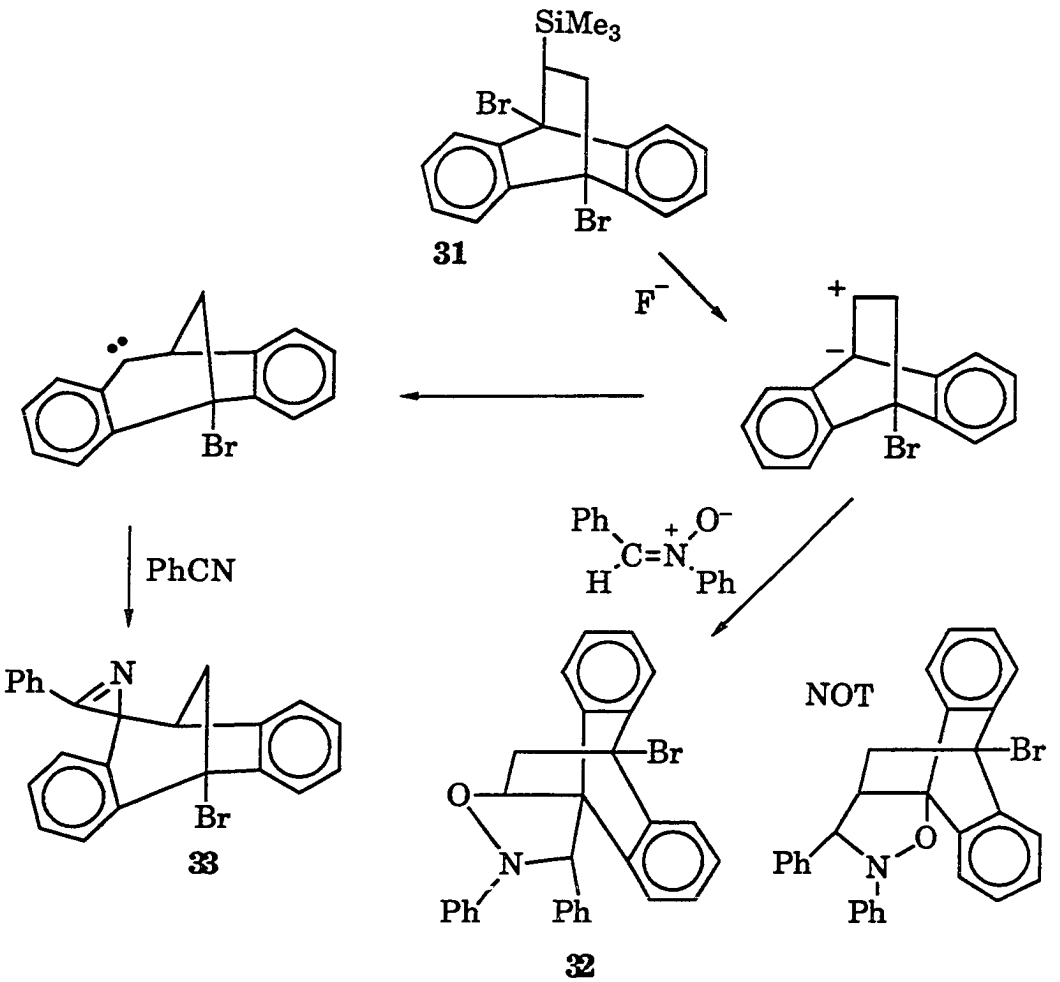
Several studies of bicyclo[2.2.2]-oct-1-ene **21** have been reported. A variety of reaction products have been attributed to the intermediacy of the Bredt olefin. In many cases the products of the reactions can be explained in terms of a stepwise mechanism.



Scheme 9

Bickelhaupt and coworkers[26] treated 1-ethoxy-2-bromobicyclo[2.2.2]octane (**28**) with *tert*-butyl lithium and concluded that the *tert*-butyl, deuterium substituted products **29** and **30** were derived from the Bredt olefin. It is, however, plausible that the products resulted from other routes (Scheme 9).

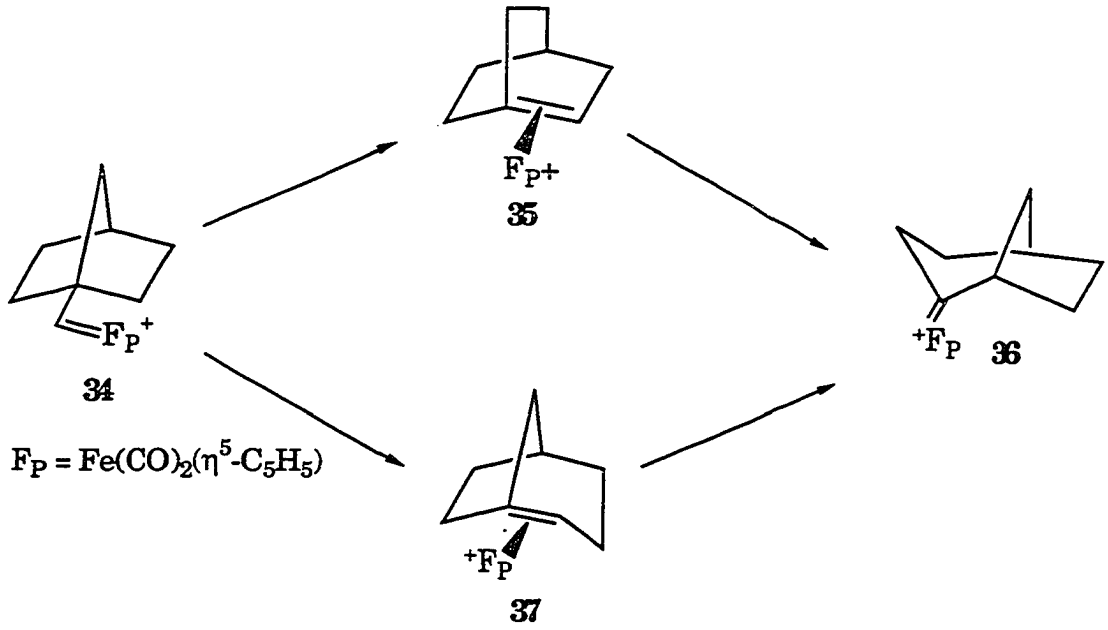
Chan and Massuda[27] report a beta-silyl bromide elimination route from the dibenzo [2.2.2] bicycle **31** which is suggestive of a dipolar intermediate



Scheme 10

trapped by diphenylnitrone to produce the adduct **32** (Scheme 10). Also, the nitrile trapped product **33** demonstrates an alkene-carbene rearrangement analogous to that observed by Barton and Yeh in the case of 1-norbornene **19** (vide supra).

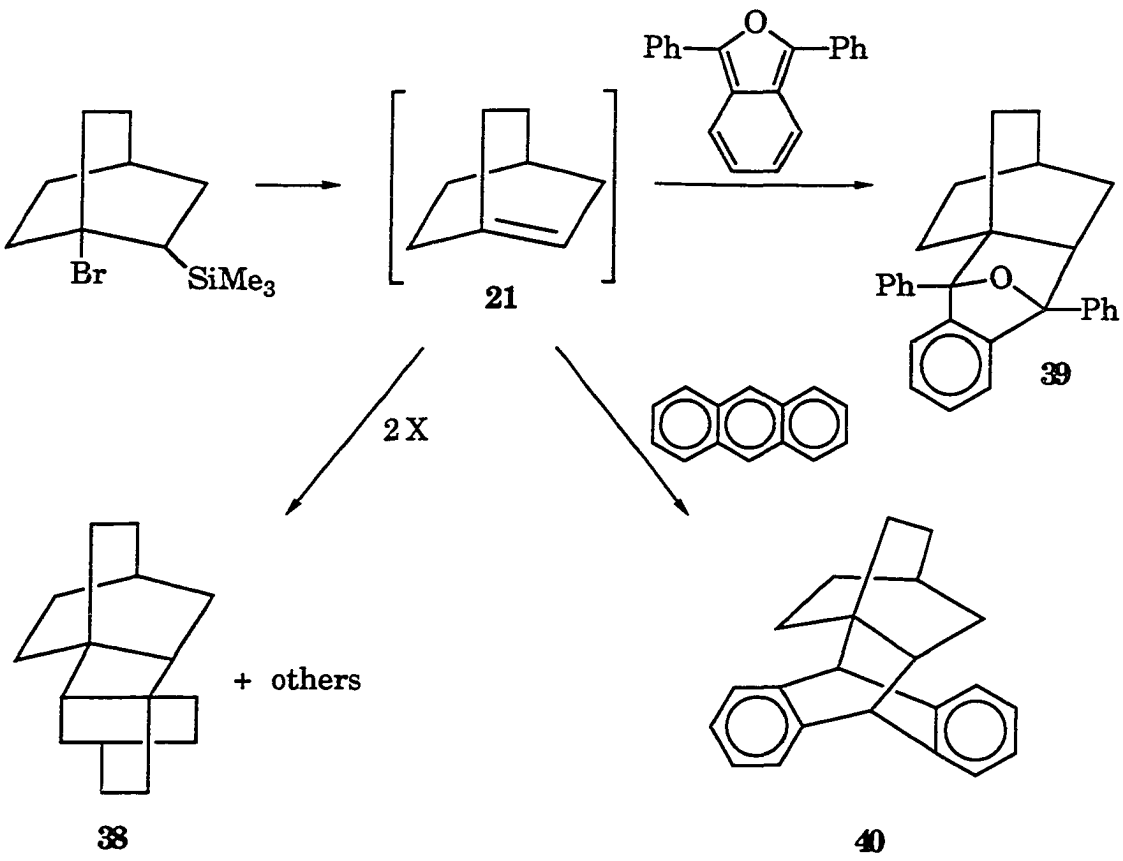
Bly et al.[28] reported the possibility of a similar rearrangement of the iron-alkylidene complex **34** (Scheme 11). A bridgehead olefin complex **35** was expected to be obtained but instead only the rearrangement product **36** was obtained.



Scheme 11

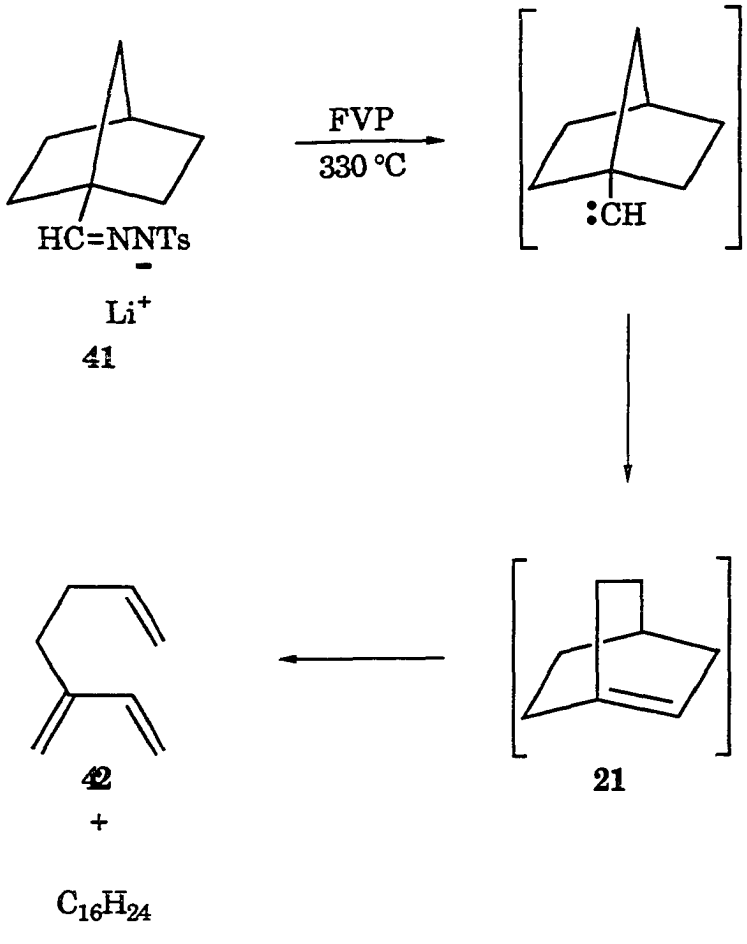
Yeh and Barton[29] used the chemistry of Chan and Massuda[24] to generate the unsubstituted [2.2.2] Bredt olefin **21** (Scheme 12).

They obtained at least three dimers of bicyclo[2.2.2]oct-1-ene **21** including the head-to-head dimer **38** as well as trapping products **39** and **40**. The X-ray crystal structures of the trapping products and the head-to-tail dimer **13** were determined (Scheme 3).



Scheme 12

The existence of these dimers was previously suggested by Wolf and Jones.[30] Compounds with the formula $C_{16}H_{24}$ were detected by GC but were characterized only as having "no [^{1}H NMR] resonances for vinyl hydrogens . . . and a parent mass of 216.187114", thus "consistent with cyclobutanes formed by dimerization of a bridgehead olefin." They proposed the bridgehead olefin as the intermediate formed in the decomposition of the lithium salt of 1-methyltosylhydrazone norbornane which then underwent a retro Diels-Alder reaction **41** to form the triene **42** (Scheme 13).

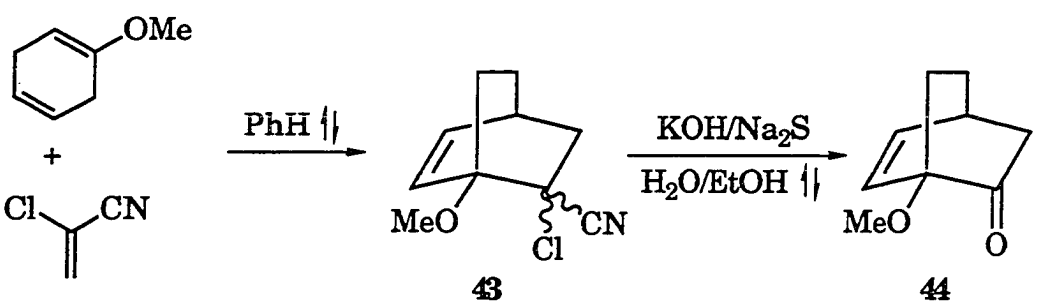


Scheme 13

RESULTS AND DISCUSSION

With this body of information as a background for our studies we undertook two endeavors: 1) to investigate the possibility of electrophilic elimination to produce the [2.2.2] Bredt olefin **1**, and 2) to demonstrate the gas-phase generation of the Bredt olefin. In both cases it was hoped that milder conditions for the elimination process could be found.

The starting material for our studies was available by the synthetic route developed by Yeh, although alterations in the strategy were adopted. The bicyclic frame was constructed using the method of Madge and Holmes.[31] Starting with the Diels-Alder reaction of 2-chloroacrylonitrile and 1-methoxy-1,4-cyclohexadiene and then oxidizing the adduct **43**,[31] the bicyclic ketone **44** was synthesized in 19% yield based on the starting diene (Scheme 14).

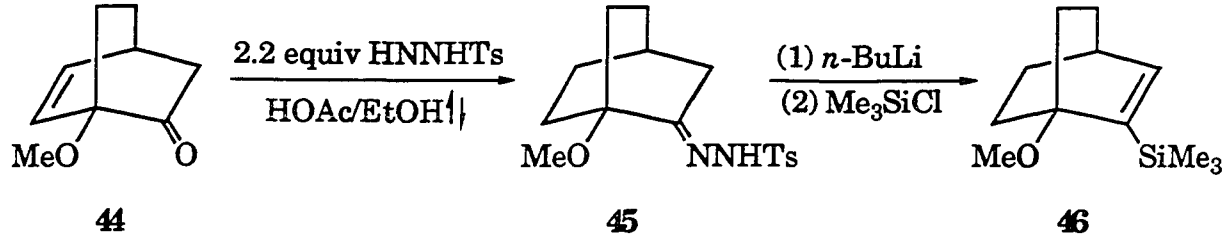


43 **44**

Scheme 14

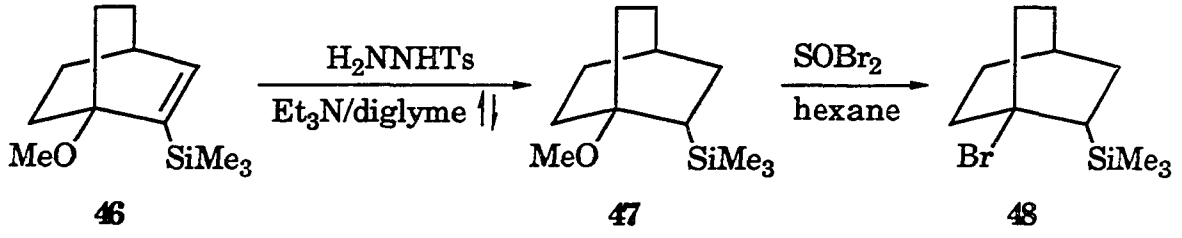
The trimethylsilyl functionality was attached *via* the hydrazone **45**. While Yeh had reduced the double bond in a separate step, it was expeditious to reduce the double bond and form the needed hydrazone in a single step. This was accomplished by treating the ketone **44** with a slight excess of the two

equivalents of tosylhydrazide theoretically needed. The purified hydrazone was then treated with 6.5 equivalents of *n*-butyl lithium in an ether solution and the vinyl anion was quenched with trimethylchlorosilane to form the silylated bicycle **46** (Scheme 15).



44 **45** **46**

Scheme 15

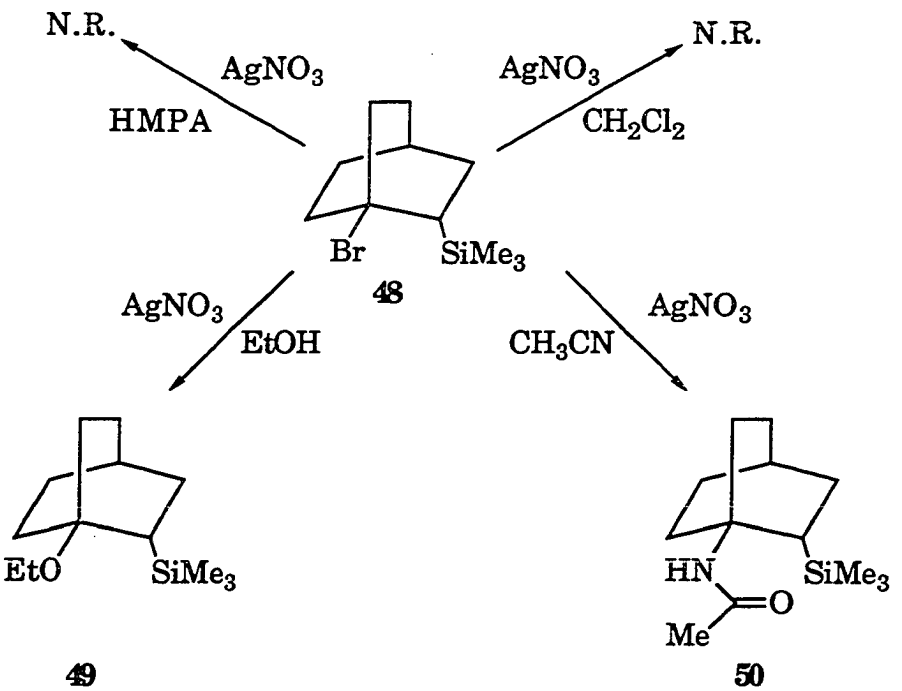


46 **47** **48**

Scheme 16

After reduction of the double bond of **46** with hydrazide to form the saturated bicycle **47**, the methoxide was converted to the bromide **48**. It was found that thionyl bromide would effect the conversion to the bromide **48** nearly quantitatively (Scheme 16).

Silver nitrate was chosen as the electrophile for the attempted elimination of trimethylsilyl bromide from **48**. The attempted reaction in methylene chloride or hexamethylphosphorus triamide gave back only starting material. However, in absolute ethanol the ethoxy substituted bicycle **49** was obtained (Scheme 17). In acetonitrile the bromide was cleanly converted in 19% yield to the amide **50**.

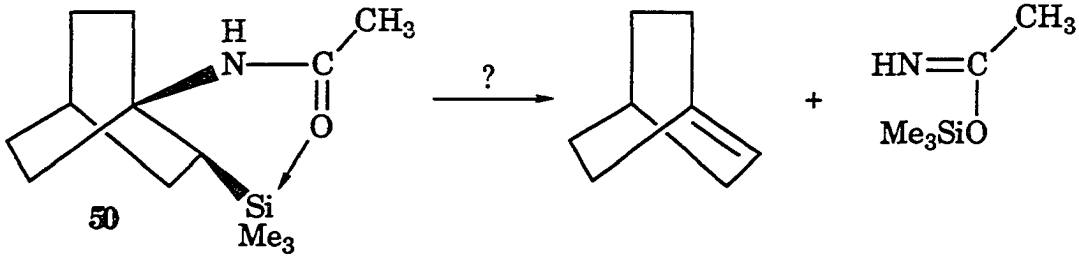


Scheme 17

Clearly the cation was formed in ethanol and acetonitrile. However, the silicon beta to the cationic center served to stabilize the charge rather than to eliminate as was desired. This result is consistent with the hyperconjugative stabilization indicated by the work of Lambert et al.[32] A rate increase of 10^{10}

due to hyperconjugation and 10^3 due to induction was established. By comparison of cyclic β-silanes with fixed conformation the dihedral angles between silicon and the leaving group was correlated to rates of solvolysis.

The acetamide **50** appeared to offer a new thermal precursor to the Bredt olefin. Although previous attempts reported by Yeh[29] to effect a thermal elimination from the methoxide **47** and bromide **48** were unsuccessful, models of the new compound suggested that it may be a better candidate due to the potential for a six-centered transition state.



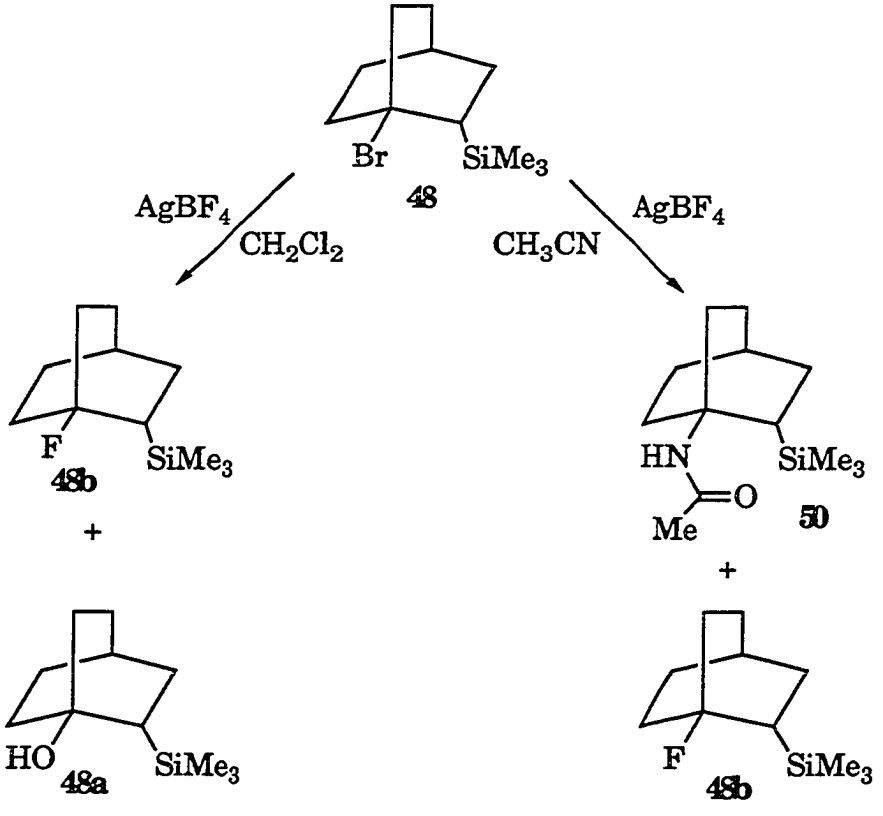
50

Flash vacuum pyrolysis at 615 °C yielded only recovered starting material and at 700 °C a myriad of twenty products was formed. Flow pyrolysis of the compound in the presence of a 100 fold excess of furan gave similar results. The (trimethylsilyl)acetamide was not observed in either case.

In hopes of facilitating the elimination process from **48** and still retaining the electrophile, silver tetrafluoroborate was used to attempt generation of the Bredt olefin.

When the reaction was carried out in methylene chloride it was found upon workup that the fluoride did not assist in elimination of the silane. The

product mixture contained products of bromide displacement by either fluoride or hydroxide giving **48a** and **48b**, respectively. No evidence of desilylation was seen. Similarly, in acetonitrile solvolysis and bromide-fluoride exchange products were observed but no evidence of the olefin was seen (Scheme 18).



Scheme 18

In hopes of generating the Bredt olefin in the gas phase, and in order to avoid competition of solvolysis with the desired elimination, it was decided to attempt the elimination on a solid supported reagent in the fashion reported by Denis for formation of strained cyclopropenes.[33]

Passing vapors of the precursor over potassium-*tert*-butoxide gave no reaction. However, when the starting material was allowed to slowly distill

over glass helices coated with a thin film of tetra-*n*-butylammonium fluoride at room temperature the trapped product stream contained the same dimers in the same ratio as were previously observed in the solution study by Yeh.[21] Although conversion was not complete, the reaction appeared to be very clean.

This represents the mildest conditions demonstrated to date for formation of the highly strained [2.2.2] Bredt olefin. Furthermore, it bears testimony to the power of the "beta effect" of silicon in the facility with which the deformed alkene is formed.

The question still remained as to the nature of the double bond formed. Previous results can still be interpreted in terms of a dipolar intermediate. Additionally, rearrangement to the carbene, as demonstrated by Chan and Massuda,[27] might be a major pathway in the reaction.

Careful visual analysis of the crystals formed in the dimerization of the Bredt olefin revealed two distinct crystal forms, and possibly a third. Mass spectra, GC retention time, and X-ray cell constants revealed the rectangular prism shaped crystals to be identical with those reported by Yeh. The platelets reveal a diastereomeric pair of *trans*-fused head-to-head dimers **51a** and **51b** (Figure 5).

The bond angles of the central cyclobutane of the head-to-tail dimer **38** (Figure 6) have increased to 89.2° and 90.8°, resulting in a very nearly planar and square four-membered ring. The angles of the head-to-head dimeric cyclobutane, however, are compressed to 86.8° and 87.2°, giving the central, four-membered ring an abnormally acute fold.

Exocyclic bond angles of dimer **38** are forced to 131.4° and 140.1° at angles C(2)-C(1)-C(7) and C(1')-C(2)-C(3), respectively, while those of dimer **51**

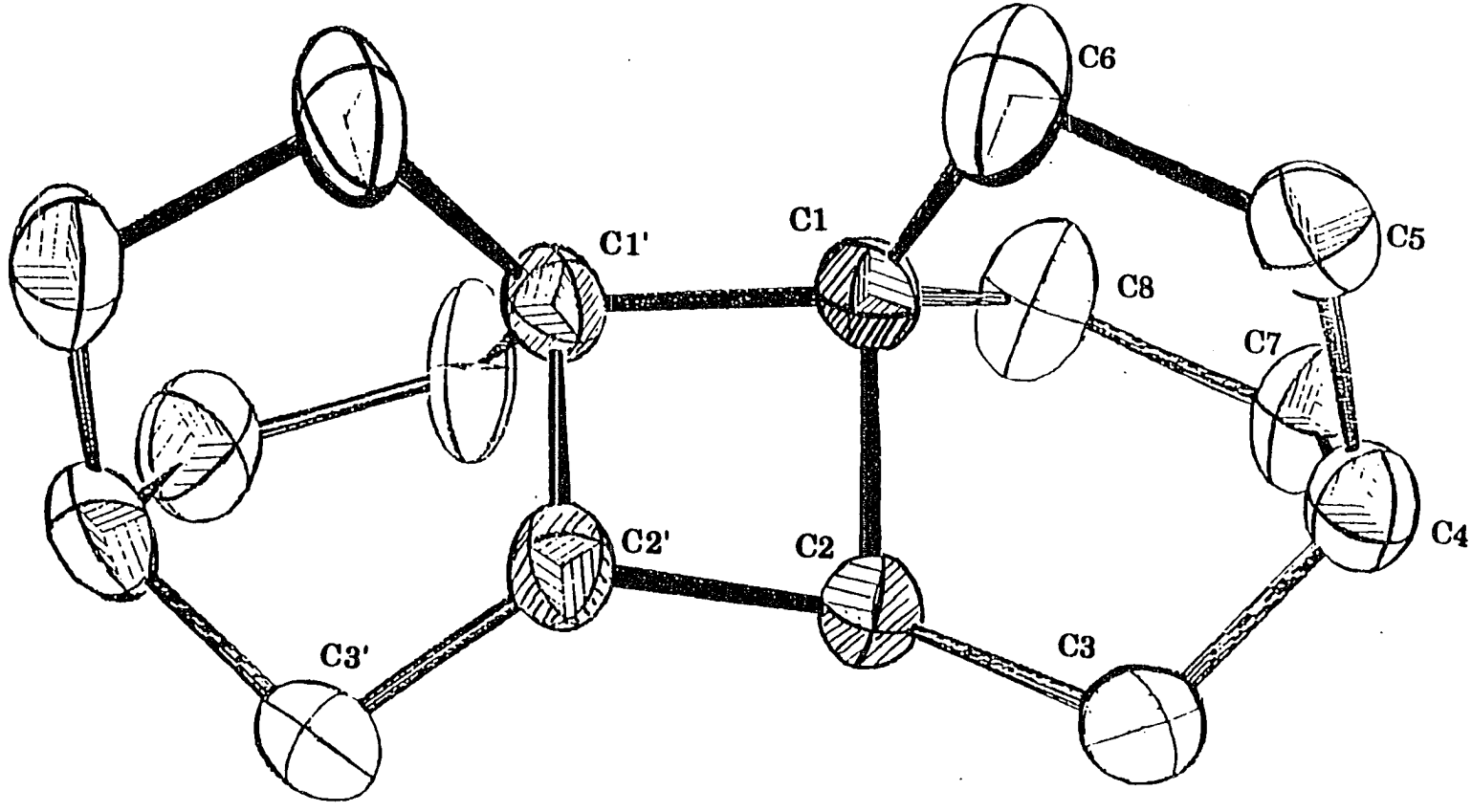


Figure 5. The head-to-head dimer of bicyclo[2.2.2]oct-1-ene **51**.

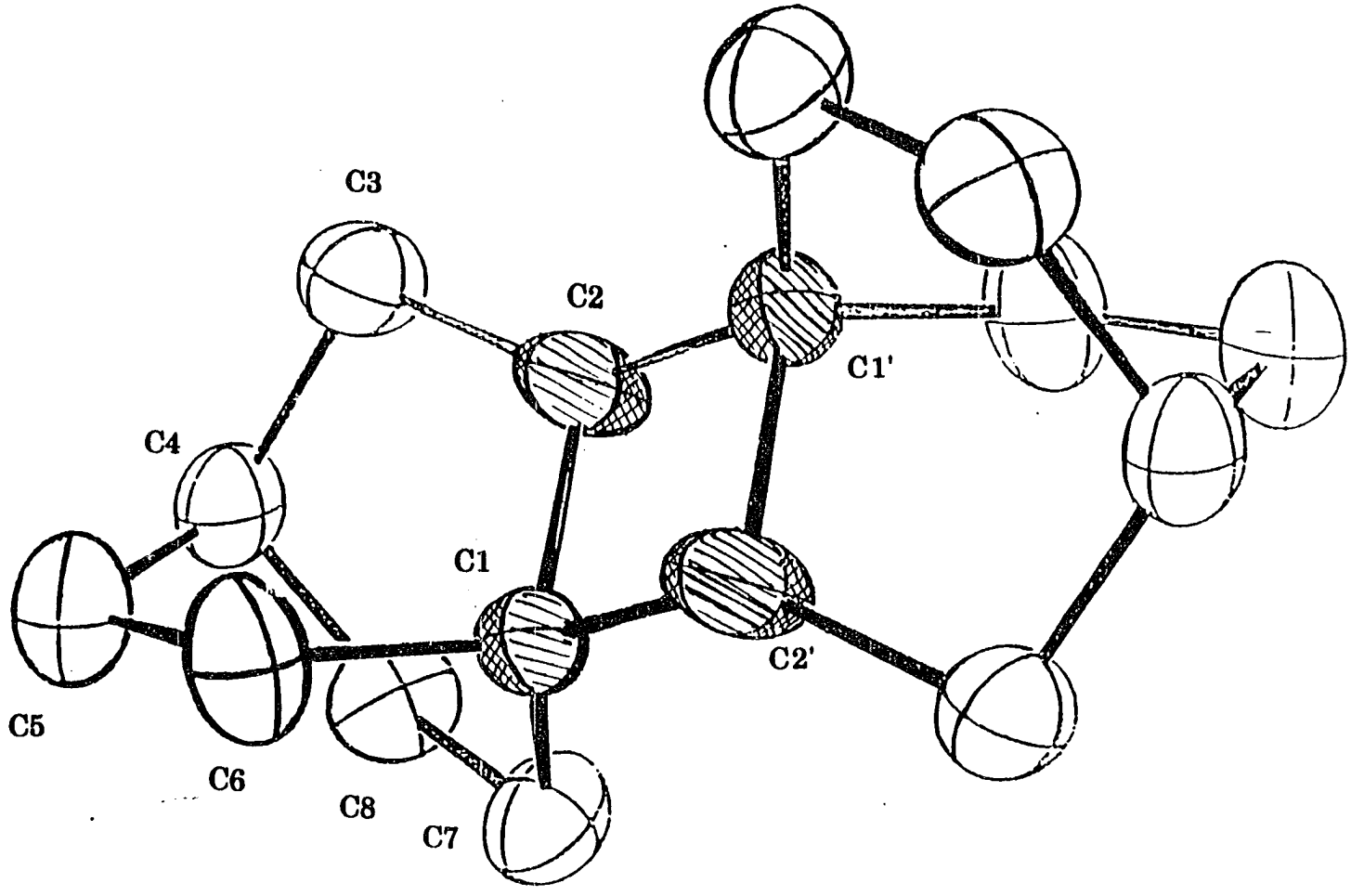


Figure 6. The head-to-tail dimer of bicyclo[2.2.2]oct-1-ene 38

Table I. Structure **38**, head-to-tail dimer

Bond Lengths (Å)		Bond Angles (°)	
C1-C2	1.534 (4)	C2-C1-C2'	089.2 (2)
C1-C2'	1.562 (4)	C2-C1-C6	111.6 (3)
C1-C6	1.540 (5)	C2-C1-C7	131.4 (3)
C1-C7	1.521 (4)	C1-C2-C1'	090.8 (2)
C2-C3	1.501 (5)	C1-C2-C3	112.0 (3)
C3-C4	1.547 (5)	C1'-C2-C3	140.1 (3)
C4-C5	1.517 (5)		
C4-C8	1.537 (5)		
C5-C6	1.528 (5)		
C7-C8	1.553 (5)		

Table II. Structure **51**, head-to-head dimer

Bond lengths (Å)		Bond Angles (°)	
C1-C1'	1.554 (4)	C1'-C1-C2	087.0 (3)
C1-C2	1.562 (7)	C2-C1-C6	118.8 (4)
C1-C6	1.520 (2)	C6-C1-C8	106.6 (3)
C1-C8	1.511 (4)	C1-C2-C2'	086.8 (4)
C2-C2'	1.566 (10)	C1-C2-C3	111.6 (5)
C2-C3	1.491 (8)	C2'-C2-C3	131.7 (7)
		C3-C2'-C3'	129.5 (7)

are stretched to 134° and 129° at C(3)-C(2)-C(2') and C(3)-C(2')-C(3'), respectively. These represent some of the largest sp^3 carbon bond angles reported. Warner's dimer **17** has bond angles of 134.5 and 132.1 at the non-bridgehead carbons of cyclobutane.[22]

The identification of the head-to-head dimers as the most abundant of the dimers along with the gas-phase generation of the Bredt olefin are strong evidence against the dipolar intermediate. Furthermore, it is demonstrated that in the case of the unsubstituted [2.2.2] Bredt olefin rearrangement to the carbene is not a major pathway.

It is bothersome that the structure of the third dimer could not be elucidated. Perhaps it would reveal the alkene to carbene isomerization.

With the Bredt olefin in hand it was interesting to consider the corresponding "Bredt allene". It would appear that no studies of this sort of compound have appeared in the literature.

Analysis of models shows a 90° bend in the allene! A molecular mechanics investigation[34] suggests a twist of 45° accompanied by a bend of 45° in the minimum geometry to an allene in the [2.2.2] system.

One of our synthetic intermediates, 1-methoxy-2-trimethylsilyl-bicyclo[2.2.2]oct-2-ene **46** was a potential precursor, so all that was required was to subject it to elimination conditions.

Thermal elimination experiments were conducted using a pulsed stirred flow reactor (SFR) modified for solution injection into the hot zone. At 500 °C very little decomposition was observed. Temperature increments of 25 °C showed increased decomposition until 575 °C at which temperature

decomposition was complete, however many products were formed even at the low conversion.

Flash vacuum pyrolysis experiments paralleled the SFR study. The starting material was recovered at 600 °C but complete conversion to a mixture of fifteen products was observed at 700 °C.

Hoping to repeat our success in producing the Bredt olefin in the gas phase the "allene precursor" **46** was passed over potassium fluoride on Chromosorb W under vacuum and, in a separate experiment, over glass helices coated with *tetra-n*-butylammonium fluoride. In both cases only starting material was recovered.

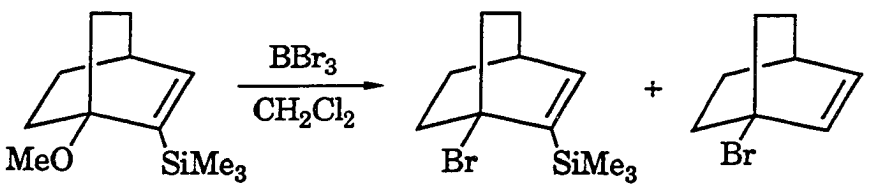
A solution of tetra-butylammonium fluoride in either DMSO or chloroform was ineffective in producing any reaction with methoxide **46** at room temperature. Solutions of potassium fluoride or of *tetra-n*-butyl ammonium fluoride in DMSO heated to 130 °C for 5 days also failed to effect any reaction.

Therefore, the methoxide **46** was transformed to the bromide **52** using the methodology applied to the saturated system. Initially, the methoxide was treated with boron tribromide in a methylene chloride solution at -78 °C and then allowed to warm to room temperature and worked up. This method was problematic and, in subsequent runs, the product decomposed before it could be isolated.

It was discovered that the reaction was complete in minutes and much of the decomposition could be avoided by simply stripping all of the volatile material from the reaction mixture, taking up the residue in hexane and

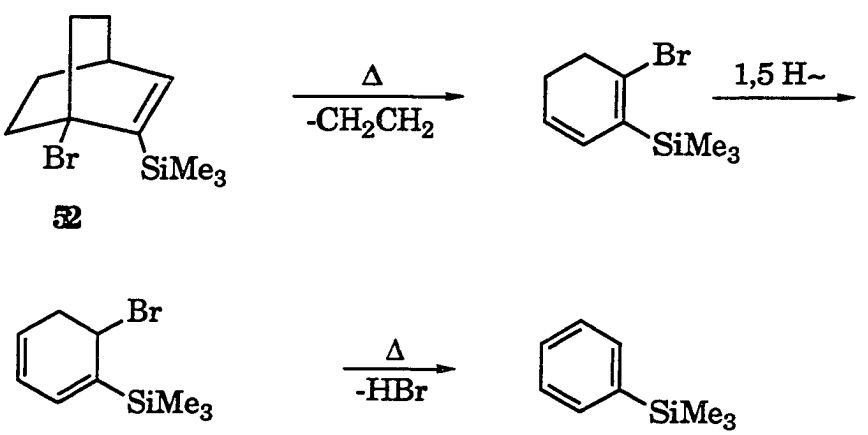
filtering out the precipitates. Removal of the hexane and preparative gas chromatography gave fair yields of the desired bromide. Desilylation of the precursor always accompanied the desired reaction (Scheme 19).

Pyrolysis of the bromide **52** in the SFR at 500 °C gave no reaction. Under



46 **52** **53**

Scheme 19



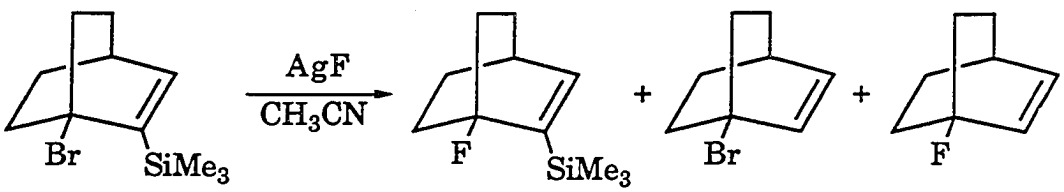
52

Scheme 20

FVP conditions at 625 °C the pyrolysate contained a 3:1 mixture of phenyltrimethylsilane and starting material. Trimethylsilyl bromide was not observed. Apparently, the precursor underwent a retro-Diels-Alder reaction followed by elimination of hydrogen bromide (Scheme 20).

In DMSO the bromide **52** failed to react with potassium fluoride at room temperature for 3 days, in a sealed tube at 100 °C for 1 day, or at 135 °C for 1 day.

The bromide **52** in acetonitrile at 130 °C gave products of desilylation and of halide substitution (Scheme 21) but no evidence of beta-elimination to give the "Bredt allene".



52 **54** **53** **55**

Scheme 21

Future studies of "Bredt allenes" may best start with calculations of a variety of systems in order to anticipate an isolable species. Several of the force field and semi-empirical calculation packages available should give useful, if crude, estimates of strain energy.

EXPERIMENTAL

Instrumentation

High resolution ^{1}H (300 MHz) and ^{13}C (75.4 MHz) nuclear magnetic resonance (NMR) spectra were recorded on Nicolet NT-300 or Varian-300 spectrometers. All chemical shifts are reported in parts per million from tetramethylsilane and the solvent used is deuterated chloroform unless stated otherwise. Designation of coupling and integration is by the standard abbreviations.

Electron impact mass spectra were recorded using a Hewlett Packard 5970B mass selective detector operating at 70eV and are reported as m/z (% relative intensity).

Infrared spectra were recorded on an IBM 98 FTIR spectrophotometer or a Hewlett Packard 5965A infrared detector and are reported in wave numbers.

Quantitative gas chromatography (GC) analyses were performed on a Hewlett Packard 5890A gas chromatograph equipped with a flame ionization detector (FID) and a recording integrator, using a 30 meter, 0.25 mm i.d., capillary column with a 0.25 μm DB-5 coating. Helium was used as the carrier gas.

Preparative gas chromatographic separations were performed on a Varian 920 gas chromatograph using 8 to 9 foot 1/4 inch copper columns packed with 15% SE-30 on chromosorb W. The instrument was equipped with a thermal conductivity detector and a chart recorder. The carrier gas was helium.

General conditions for flash vacuum pyrolysis (FVP)

All samples were vacuum distilled from a bath maintained at a temperature allowing the slow introduction of the sample into a horizontal quartz tube packed with irregular sized quartz chips and heated with an electric tube furnace. The 1.6 cm x 30 cm heated zone of the quartz tube was maintained at constant temperature by a temperature controller. Pyrolysates were collected in a cold trap cooled by liquid nitrogen. Pressures were measured with an ionization gauge behind two liquid nitrogen traps and are, therefore, only reflective of the actual pressures in the pyrolysis zone.

General conditions for flow pyrolyses

The oven and furnace were the same as used for the FVP with the exception that the tube was positioned vertically rather than horizontally. The pyrolysis tube was swept with a 40 mL/min stream of nitrogen throughout the addition unless otherwise specified. The pyrolysates were collected in a trap cooled by dry ice.

General conditions for stirred-flow reactor (SFR) pyrolyses

The pulsed stirred-flow reactor used was a modification of the design of Baldwin et al.[35] A 3 cm^3 quartz reactor, swept by a stream of helium, was maintained at constant temperature by a Digi-Sense temperature controller. The reactor was ported for syringe-injected introduction of liquid samples into the hot-zone. The product stream was fed into the injection port of a Hewlett Packard 5890A gas chromatograph equipped with serially configured Hewlett Packard 5970B mass selective (MSD) and 5965A infrared detectors (IRD).

Similarly, an SFR was connected to a GC equipped with parallel configured FID and MSD.

Synthesis of 1-methoxybicyclo[2.2.2]oct-5-en-2-one, 44

A 500 mL round-bottom flask fitted, with a Friedrichs condenser and a magnetic stirring bar was charged with 160 g 1-methoxy-1,4-cyclohexadiene (1.2 mol-Aldrich, 85%) and 125 g 2-chloroacrylonitrile (1.4 mol-Aldrich, 99%) dissolved in 260 mL benzene (Fisher, ACS). The solution was refluxed 20 hours.

After removing the solvent by rotary evaporation the crude Diels-Alder adduct **43** was carefully added *via* pressure equalizing dropping funnel to an oxidation mixture prepared by refluxing for 20 hours a mixture of 270 g sodium sulfide (1.1 mol-Fisher, ACS) and 70 g potassium hydroxide (1.1 mol-Fisher, ACS) in 1.5 L 60% ethanol, all in a 2 L three-neck round-bottom flask equipped with a Friedrichs condenser and mechanical stirrer. The resulting solution was refluxed 12 hours, at which time GC analysis showed complete conversion to 1-methoxybicyclo[2.2.2]oct-dien-2-one **44**.

The reaction mixture was cooled to room temperature and divided into two portions. Each portion was poured over 100 g ice and was extracted with 200 mL benzene/ether (1:3). The extract was washed with 200 mL each water, dilute hydrochloric acid, and, again, water. The solvents were removed from the combined extracts by rotary evaporation at elevated temperature (ca. 100 °C) after drying over anhydrous sodium sulfate. The amber residue was vacuum distilled (85 °C/0.8 mmHg) yielding 39.3 g **44** (19% yield based on 1-methoxy-1,4-cycolohexadiene). The identity of the ketone was confirmed by

spectra: ^{1}H NMR 6.39 (dd, 1H, J=6.3, J=8.4), 6.19 (d, 1H, J=6.3), 3.45 (s, 3H), 2.88 (m, 1H), 2.05 (dd, 2H, J=2.7, J=1.2), 1.57-1.84 (m, 4H); ^{13}C NMR 209.9, 135.8, 129.5, 84.6, 53.1, 40.2, 31.5, 26.6, 25.2; FTIR 2962(s), 1752(s), 1615(w), 1177(m), 1082(m); MS 152 (M^+, 1), 124(26), 110(100), 109(83), 95(23), 79(29), 67(26), 53(32).

Synthesis of 1-methoxybicyclo[2.2.2]octan-2-one *para*-tosylhydrazone, **45**

A 9.9 g aliquot of the ketone, **44** (59 mmol-91%), was dissolved in a suspension of 23.3 g *p*-toluenesulfonhydrazide (125 mmol-Aldrich, 97%) in 180 mL absolute ethanol and 15.4 mL glacial acetic acid (Fisher), all in a 500 mL round-bottom flask equipped with a Friedrichs condensor and a magnetic stirring bar. After refluxing 20 hours, the mixture was cooled in an ice bath and the crystals thus formed were isolated by vacuum filtration, washed with cold absolute ethanol, and air-dried. Double recrystallization from absolute ethanol afforded 15.3 g **45** (48.7% yield, M.P.=171.5-174 °C). The hydrazone **45** was identified by the spectral data: ^{1}H NMR 7.84 (d, 2H, J=8.4), 7.25 (d, 2H, J=8.4), 3.17 (s, 3H), 2.37 (s, 3H), 2.19 (d, 2H, J=1.5), 1.91 (t, 1H, J=1.5); ^{13}C NMR 162.1, 143.9, 135.4, 129.4, 128.2, 75.0, 51.4, 33.4, 29.0, 25.7, 25.6, 21.6. An additional 5.2 g of the hydrazone was obtained by similar treatment of the mother liquor.

Synthesis of 1-methoxy-2-(trimethylsilyl)bicyclo[2.2.2]oct-2-ene, **46**

The hydrazone **45** (15.3 g - 47.5 mmol) was dissolved in 150 mL ethyl ether (Fisher, ACS) in an oven-dried, argon flushed 500 mL round-bottom flask equipped with a magnetic stirring bar and pressure equalizing dropping funnel. To this solution was added at room temperature, over a 2 hour period,

126 mL 2.5 M *n*-butyl lithium (6.5 equivalents-Aldrich, in hexanes). The resulting clear-brown solution was quenched by slow (45 min.), syringe addition of 49.8 g trimethylchlorosilane (Aldrich, 98%). This mixture was left stirring for 12 hours.

The cooled (ice bath) reaction mixture was quenched with 50 mL 10% ammonium chloride and was washed with 50 mL each water, saturated sodium bicarbonate, and, again, water. The combined aqueous layers were extracted with 50 mL ether and the combined organic layers dried over anhydrous sodium sulfate. Removal of the solvent by rotary evaporation left 21.5 g clear-yellow residue which was reduced without further purification.

An aliquot of vinyl silane **45** was purified by preparative GC to obtain the spectral data: ^{1}H NMR 6.35 (d, 1H, J=6.6), 3.22 (s, 3H), 2.37 (m, 1H), 1.88 (dt, 2H, J=3.6, J=10.7), 1.51 (ddt, 2H, J=9.3, J=3.6, J=1.8), 1.29 (m, 2H), 1.02 (m, 2H), 0.87 (tt, 1H, J=1.8, J=7.2), -0.05 (s, 9H); ^{13}C NMR 151.5, 140.9, 80.7, 49.1, 30.1, 27.3, 26.0, -0.5; FTIR 2954(s), 1252(w), 1121(m), 1072(m); MS 211(2.7), 210 (M^{+}, 24.4), 195(12), 182(100), 167(28), 137(20), 89(32), 75(49).

Reduction of 1-methoxy-2-(trimethylsilyl)bicyclo[2.2.2]oct-2-ene to 1-methoxy-2-(trimethylsilyl)bicyclo[2.2.2]octane, **47**

To a suspension of 10 g *p*-toluenesulfonhydrazide (54 mmol-Aldrich, 97%) in 80 mL diglyme (Kodak, 99%) and 11.2 g triethyl-amine (Kodak, ACS, dried over sodium hydroxide) was added 21.5 g of the crude bicyclic alkene **46**, all in a 250 mL round-bottom flask equipped with a magnetic stirring bar and a Friedrichs condensor. The mixture was refluxed for 20 hours.

The reaction mixture was stripped of diglyme by rotary evaporation at 100 °C. The clear-amber residue was partitioned between 100 mL each water and ether. The organic layer was washed with 50 mL dilute hydrochloric acid and 50 mL water followed by drying over anhydrous sodium sulfate. Removal of the solvent followed by vacuum distillation (60-70 °C/7 mmHg) gave 4.2 g of the saturated bicycle **57**. The compound was identified by its ^{1}H NMR 3.07 (s, 1H), 1.56 (m, 10H), 0.03 (s, 1H), 0.00 (s, 9H); MS 212 (M^+, 5), 198 (3), 197 (20), 139 (7), 89 (95), 79 (54), 73 (100), 59 (51).

Synthesis of 1-bromo-2-(trimethylsilyl) bicyclo[2.2.2]octane **48**

In an oven-dried, argon flush 50 mL round bottom flask 12.40 g thionyl bromide (60 mmol-Aldrich, 99%) and 4.16 g 1-methoxy-2-trimethylsilyl bicyclo[2.2.2]octane **47** were combined at room temperature. The mixture was stirred twelve hours and then slowly poured over ice chips (ca. 20 g) and the mixture was then partitioned with 20 mL pentane. The pentane extract was washed twice with 20 mL water, with 20 mL saturated sodium bicarbonate, and, again, with water. After drying over anhydrous sodium sulfate the solvent was removed leaving 4.40 amber oil (87% pure by GC-99% yield). The bromide **48** gave the following spectra: ^{1}H NMR 2.18-2.24 (m, 2H), 1.59-1.81 (m, 10H), 0.10 (s, 9 H); ^{13}C NMR 70.6, 42.8, 36.3, 34.8, 32.8, 29.5, 28.9, 23.6, -0.6; MS 247 (0.4), 245 (M^+-15, 0.5), 149 (16), 139 (32), 137 (32), 107 (27), 93 (56), 79 (100), 73 (72), 66 (93).

Attempted silver-induced elimination of trimethylsilylbromide from 1-bromo-2-(trimethylsilyl)bicyclo[2.2.2]octane 48

Method A: A mixture of 44 mg of the bicyclic silane **48** (0.17 mmol) and 84 mg silver nitrate (0.5 mmol-Baker, ACS) in 9.2 mL dry hexamethylphosphorustriamide was stirred at room temperature for 24 hours. The reaction mixture was partitioned between 10 mL each water and carbon tetrachloride and the organic layer washed three times with 10 mL portions of water. MSD showed only the starting bicycle.

Method B: A mixture of 21 mg of the bicyclic silane **48** (0.17 mmol) and 65 mg silver nitrate (0.4 mmol Baker, ACS) in 1 mL methylene chloride (Fisher, ACS) was stirred at room temperature for 24 hours. The solvent was stripped and replaced with carbon tetrachloride and the mixture was filtered to remove the salt. MSD showed only the starting bicycle.

Method C: A mixture of 49 mg of the bicyclic silane **48** (0.19 mmol) and 65 mg silver nitrate (0.4-Baker, ACS) in 1.0 mL acetonitrile was stirred at room temperature for 24 hours. The reaction mixture was partitioned between pentane and water and the organic portion washed with brine. The bromide was cleanly converted to the 1-acetamide-2-trimethylsilylbicyclo[2.2.2]octane **50**. (Characterization is included with the scaled-up synthesis which follows.)

Method D: A mixture of 45 mg of the bicyclic silane **48** (0.17 mmol) and 65 mg silver nitrate (.4 mmol-Baker, ACS) in 1.0 mL ethanol was stirred at room temperature for 24 hours. The reaction mixture was partitioned between pentane and water and the aqueous layer extracted with pentane. The combined organic layers were washed several times with brine and dried over

anhydrous sodium sulfate. After removing the solvent by rotary evaporation the residue was purified by preparative GC for spectra.

Method E: A mixture of 11 mg of the bicyclic silane **48** (0.04 mmol) and 22 mg silver tetrafluoroborate (0.11 mmol-Alfa) in 1 mL wet methylene chloride was stirred at room temperature for 30 minutes. After filtering the reaction mixture through a pipette plugged with anhydrous magnesium sulfate the products' structures were assigned on the basis of their mass spectra. 1-Hydroxy-2-(trimethylsilyl)bicyclo[2.2.2]octane **48a** gave MS 198 (M^+, 11), 183 (6), 126 (48), 108 (47), 107 (20), 91 (43), 79 (95), 75 (100), 67 (58). 1-Fluoro-2-(trimethylsilyl) bicyclo[2.2.2]octane **48b** gave MS 185 (M^+-15, 1), 108 (14), 107 (36), 93 (100), 91 (26), 80 (81), 79 (85), 73 (69), 67 (45).

Method F: A mixture of 12 mg of the bicyclic silane **48** and 13 mg silver tetrafluoroborate in 0.4 mL acetonitrile was stirred at room temperature for 4 hours. The reaction mixture was filtered through a plug of anhydrous magnesium sulfate with the aid of 1 mL carbon tetrachloride. Structures were assigned based on mass spectra. The fluoride **48b** gave the same mass spectra as described in method B above and the mass spectrum acetamide **50** was compared to an authentic sample.

The generation of bicyclo[2.2.2]oct-1-ene **51**

Glass helices coated with tetra-*n*-butyl ammonium fluoride were prepared by stripping the solvent from a well stirred mixture of 30 g glass helices and 3 g tetra-*n*-butyl ammonium fluoride trihydrate (Aldrich, 99%) in 30 mL methylene chloride (Fisher, ACS). A 6 cm x 1 cm glass column was packed with the helices was evacuated to 10^{-5} mmHg at room temperature for 4

hours. A 250 mg aliquot of the bicyclic silane **48** was slowly introduced at 10^{-5} mmHg and the product stream collected in a liquid nitrogen cooled receiving flask. GC-MS analysis of the product shows incomplete, but clean, conversion to the same dimers reported by Yeh.[29]

The low boiling material was removed from the product mixture at room temperature and high vacuum (ca. 0.2 mmHg). The residue was recrystalized from hot ethanol leaving 38 mg white crystals (36% yield). The following spectra were obtained from the mixture: ^{1}H NMR 0.8-2.2 (m); ^{13}C NMR 23.9-49.2 (24 peaks). The head-to-tail dimer gave the following spectra: FTIR 2944(s), 2870(m), 1462(w); MS 216 (M^+, 11), 201 (5), 187 (32), 159 (13), 145 (16), 131 (19), 119 (23), 105 (41), 91 (84), 79 (100). Exact mass for $C_{16}H_{24}$, calc'd 216.18780, found 216.18799 (-0.9 ppm). Crystallographic data for the head-to-tail dimer **38** are: $C_{16}H_{24}$, monoclinic, $P2_1/n$, a=6.407 (1) Å, b=13.187 (3) Å, c=7.234 (2) Å, β=97.79 (2)°, V=605 Å^3, Z=2, d calcd. = 1.187 g/cm^3, $\mu(MoK_\alpha)$ = 0.613 cm^{-1}, 0.20 x 0.28 x 0.18 mm, θ-2θ scan, 3023 reflections collected, three strong reflections measured hourly indicating 18.3% intensity loss so decay correction applied, 1875 observed redundant data average gave 3.2% agreement factor (on F_{OBS}), 780 unique data, 443 with $F_{OBS}^2 > 3\,\sigma(F_{OBS}^2)$, direct methods, R = 0.0550, R_w = 0.0694. The head-to-head dimer gave the following spectra: FTIR 2939(s), 2870(m), 1458(w); MS 217 (8), 216 (51), 201 (7), 187 (60), 159 (27), 145 (27), 131 (41), 119 (31), 105 (49), 91 (95), 79 (100). Exact mass for $C_{16}H_{24}$, calc'd 216.18780, found 216.18835 (+ 2.52 ppm). Crystallographic data for the head-to-head dimer **51** are: $C_{16}H_{24}$, monoclinic, $P2_1/c$, a=8.642 (2) Å, b=11.785 (2) Å, c=12.359 (2) Å, β=104.83 (2)°, V=1216.8 (3) Å^3, Z=4, d calcd. = 1.181 g/cm^3, $\mu(CuK_\alpha)$ = 0.478 mm^{-1}, 0.30 x 0.18 x 0.12 mm, θ-2θ scan, 3519 reflections collected, three strong

collections measured hourly indicating 2% intensity loss to decay so correction applied, 3515 observed redundant data average gave 2.5% agreement factor (on F_{OBS}), 1630 unique data, 1315 with $F_{OBS}^2 > 2\sigma(F_{OBS}^2)$, direct methods, R=0.0633, R_2=0.0712. The "other dimer" gave the following spectra: FTIR 2936(s), 2870(m), 1458(w); MS 216 (M^+, 14), 201 (6), 187 (42), 159 (18), 145 (19), 131 (23), 119 (25), 105 (44), 91 (85), 79 (100). Crystal structures were obtained for the head-to-head and head-to-tail dimers.

Synthesis of 1-acetamide-2-(trimethylsilyl)bicyclo[2.2.2]octane, **50**

An oven dried 50 mL round-bottom flask was charged with 1.146 g 1-bromo-2-(trimethylsilyl)-bicylo[2.2.2]-octane **48** (4.4 mmol), 1.054 g silver nitrate (6.2 mmol-Baker, ACS), and 30 mL acetonitrile (Fisher, ACS). After stirring for 4 hours at room temperature the reaction mixture was portioned between pentane and water (30 mL each) and the organic layer washed with two 20 mL portions of brine. The solvent was stripped from the dried extract leaving 0.207 g (19.7% yield) of the acetamide. The structure of 1-acetamide-2-(trimethylsilyl)bicyclo[2.2.2]octane, **50** was based on the spectral data: ^{1}H NMR 2.004 (s, 1H), 1.42-1.9 (m, 11H), 0.018 (s, 1H), -0.007 (s, 9H); ^{13}C NMR 172.7, 55.8, 32.3, 30.8, 29.1, 26.3, 26.0, 24.3, -1.4, -1.7; FTIR 3455(w), 2938(s), 2875(m), 1710(s), 1494(s), 1255(m), 839(m); MS 241 (1), 240 (11), 239 (M^+, 60), 238 (13), 224 (86), 210(100), 168(40), 132(43), 116(65), 75(37), 73(96).

Flash vacuum pyrolysis of 1-acetamide-2-(trimethylsilyl)bicyclo[2.2.2]octane **50**

The amide **50** was pyrolyzed in the standard fashion at 615 °C, 700 °C, and 800 °C and 10^{-4} mmHg. At 615 °C the compound was stable. At 700 °C the

compound began to decompose to many (more than twenty) products. At 800 °C the decomposition was complete. The mixture of products was not separated or identified.

Flow pyrolysis of 1-acetamide-2-(trimethylsilyl)bicyclo[2.2.2]octane **50**

A solution of 43 mg **50** in 1.0 mL furan was prepared. Aliquots of the solution were slowly introduced to the flow system at 550 °C and at 650 °C. In the former case the amide was stable but in the latter an intractable mixture of more than fifteen products was formed.

Attempted fluoride-induced elimination of trimethylmethoxysilane from 1-methoxy-2-(trimethylsilyl)bicyclo[2.2.2]oct-2-ene **46**

Method A: An NMR tube was charged with a 30 mg aliquot of the bicyclic silane **46** (140 mmol), 24 mg tetra-*n*-butyl ammonium fluoride, trihydrate (76 mmol-Aldrich, 99%) and 1 mL deuterated chloroform. The solution was left standing at room temperature and monitored daily by ^{1}H NMR. No reaction was evident after seven days.

Method B: An NMR tube was charged with 9 mg (42 mmol) of the bicyclic silane **46**, 6.5 mg tetra-*n*-butyl ammonium fluoride, trihydrate (20 mmol) and 1 mL deuterated dimethylsulfoxide. Monitoring by ^{1}H NMR showed no reaction after seven days.

Method C: An NMR tube was charged with 10 mg of the bicyclic silane **46** (48 mmol), 3 mg anhydrous potassium fluoride (52 mmol-Aldrich, 99%), and 0.7 mL deuterated dimethyl sulfoxide. A 0.1 mL aliquot of water was

added to enhance the solubility of the potassium fluoride. No reaction was evident after seven days of ^{1}H NMR monitoring.

Method D: A degassed mixture of 9 mg of the bicyclic silane **46** (43 mmol), 14 mg tetra-*n*-butyl ammonium fluoride trihydrate (45 mmol), and 1 mL deuterated dimethyl sulfoxide was sealed in an NMR tube and heated at 130 °C for five days. ^{1}H NMR showed no reaction.

Method E: A 6 cm x 1 cm glass column was packed with a well commingled mixture of potassium fluoride and 80-100 mesh non-acid washed chromosorb W (50:50, wt:wt). The column was evacuated and heated to 75 °C for 1 hour. A 349 mg sample of the bicyclic silane **46** was then introduced at 10^{-5} mmHg over a 20 minute period. Material passing through the column was trapped in a liquid nitrogen cooled receiving flask. Only starting material (239 mg - 68.5% mass recovery) was recovered. There was no evidence of decomposition products.

Method F: Under an argon atmosphere 30 g 0.25 inch glass helices, 3.0 g tetra-*n*-butyl ammonium fluoride, trihydrate and 30 mL dry methylene chloride were combined in a flame dried 100 mL round-bottom flask. After vigorous stirring the solvent was stripped at reduced pressure leaving salt coated, glass helices.

As described in method E, 300 mg of the bicyclic silane **46** was passed through a tube packed with the tetra-*n*-butyl ammonium fluoride trihydrate coated helices. No decomposition products were present in the trapped material (178 mg - 59.3% mass recovery).

Pyrolysis of 1-methoxy-2-(trimethylsilyl)bicyclo[2.2.2]oct-2-ene **46**

Method A: Aliquots of 0.1 μL of the bicyclic silane were injected into an SFR and the reaction checked by GC-FID. The temperature was increased from 500 °C to 575 °C at 25 °C increments. Very little decomposition was observed at 500 °C, but most of the starting material was consumed at 575 °C. A myriad of products were formed.

Method B: A 298 mg aliquot of the bicyclic silane **46** was subjected to FVP at 600 °C and 10^{-3} mmHg. Only starting material was recovered. A 222 mg sample was subjected to FVP in 700 °C and 10^{-3} mmHg. The pyrolysate consisted of fifteen products including tetramethylsilane, methoxytrimethylsilane, toluene, phenyltrimethylsilane, phenoxytrimetylsilane, and trimethylsilyltoluene which were identified by GC/MS.

Synthesis of 1-bromo-2-(trimethylsilyl)-bicyclo[2.2.2]oct-2-ene **52**

A 275 mg aliquot of 80% 1-methoxy-2-(trimethylsilyl)bicyclo[2.2.2]oct-2-ene **46** (1 mmol) was dissolved in 5 mL methylene chloride and cooled to -78 °C in an oven-dried 25 mL round-bottom flask equipped with a magnetic stirrer and under an argon atmosphere. Over a 60 minute period 1.45 mL 1.0 M boron tribromide (1.45 mmol-Aldrich, in hexane) was added via syringe. The solution was allowed to warm to room temperature.

After stirring at room temperature for 2 hours the mixture was cooled to 0 °C and quenched with 2 mL water. The mixture was washed with three 20 mL portions of water and the organic material dried over 4 Å molecular sieves. The solvent was stripped by rotary evaporation leaving 279 mg of a clear-amber

liquid which was a 1:1.5 the desired product and 1-bromo-bicyclo[2.2.2]oct-2-ene. The product gave **52** the following spectra: ^{1}H NMR 6.56 (d, 1H, J=6), 2.50 (m, 1H), 2.09-2.22 (m, 2H), 1.59-1.91 (m, 2H), 1.66 (t, 2H, J=12); 1.34 (t, 2H, J=12); ^{13}C NMR 145.6, 144.3, 38.9, 38.0, 28.3, 27.9, -0.1; FTIR 2956(s), 2877(w), 1255(m), 1063(w), 848(s); MS 260(1), 258(M^+, 1), 245(54), 243(53), 217(11), 215(12), 163(48), 139(100), 137(99), 105(72), 91(16), 78(13), 73(42). The desilylated by-product **53** gave the following spectra: FTIR 2960(s), 2878(m), 1459(w), 995(m), 853(w); MS 188(8), 186(M^+, 9), 160(64), 158(69), 107(17); 91(14), 79(100), 77(36).

Attempted fluoride-induced elimination of trimethylsilyl bromide from 1-bromo-2-(trimethylsilyl)bicyclo[2.2.2]oct-2-ene **52**

A 75 mg aliquot of the bromosilane **52**, 17 mg potassium fluoride, and 2.5 mL deuterated dimethylsulfoxide were combined in an NMR tube. No reaction was apparent by ^{1}H NMR after 72 hours. The tube was heated to 100 °C for 24 hours but still, no reaction was evident. After heating a 135 °C for an additional 24 h no reaction was evident. The tube exploded upon heating to 165 °C.

Reaction of 1-bromo-2-(trimethylsilyl)bicyclo[2.2.2[oct-2-ene **52** with silver fluoride

A mixture of 165 mg bromo-2(trimethylsilyl)bicyclo[2.2.2]oct-2-ene **52** (0.6 mmol), 262 mg silver fluoride (2.1 mmol-Alfa), and 3 mL acetonitrile (Fisher, dried over 3 Å molecular sieves) were placed in a tube, degassed and sealed. After 3 days at 110 °C the tube was cooled and opened. Salts were filtered out through a plug of anhydrous magnesium sulfate. The filtrate was analyzed by

GC/IR/MS. Product **A** gave the following spectra: MS 126 (M^+, 6), 98 (100), 97 (50), 85 (4), 77 (9), 57 (4), 51 (8); FTIR 3061(w), 2962(s), 2883(m), 1613(w), 1373(w), 1141(m), 1087(w). Product **B** gave the following spectra: MS 188 (8), 186 (9), 160 (64), 158 (69), 107 (17), 91 (14), 79 (100), 77 (36); FTIR 2960(s), 2878(m), 1459(w), 995(m), 853(w). Product **C** gave the following spectra: MS 184 (1), 183 (8), 170 (4), 105 (18), 91 (5), 78 (14), 77 (100), 73 (8); FTIR 3029(w), 2960(s), 2879(m), 1324(w), 1254(m), 1100(m), 848(s).

Pyrolysis of 1-bromo-2-(trimethylsilyl)bicyclo[2.2.2]oct-2-ene **52**

Method A: A 5% solution of the bromosilane in pentane was injected into the SFR in 2 μL aliquots a 500 °C, 550 °C, and 600 °C resulting in decomposition of 10%, 50%, and 100%, respectively, of the starting material. FID and MSD monitoring showed clean conversion to phenyltrimethylsilane.

Method B: The bromosilane (53 mg) was subjected to FVP at 625 °C and 10^{-4} mmHg over a 15 min period. The pyrolysate contained 22% starting material and 78% phenyltrimethylsilane. Mass recovery was not determined. Phenyltrimethylsilane was identified by match of its GC retention time and mass spectral comparison to an authentic sample.

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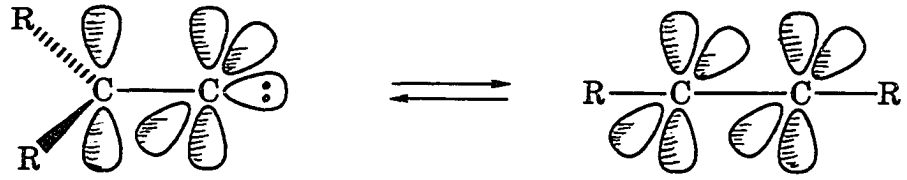
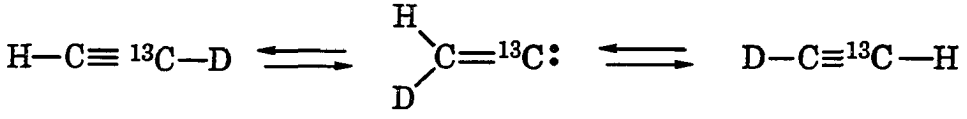
PAPER II. THE GENERATION AND REARRANGEMENTS OF BICYCLIC ALKYLIDENE CARBENES

LITERATURE REVIEW

Intramolecular rearrangement of vinylidenes to form acetylenes is a very facile process. The α-β bond length is short and the groups on the β-carbon are coplanar with the vacant p-orbital of the α-carbon, thus the path for the migration of R is readily accessible (Scheme 1).

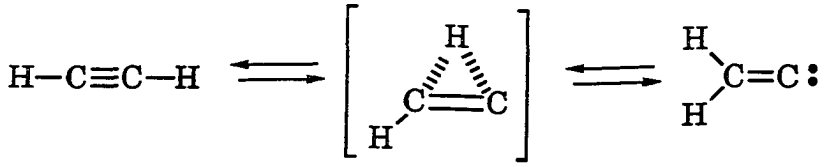


Scheme 1



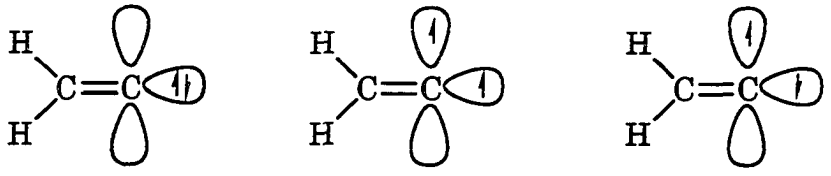
Scheme 2

In the simplest case, that of acetylene, the scrambling of doubly labelled acetylene is attributed to an intermediate vinylidene[1] (Scheme 2). A 3 kcal mol^{-1} barrier to isomerization is predicted by *ab initio* calculation.[2] A transition state involving a three-membered ring has been proposed (Scheme 3).



Scheme 3

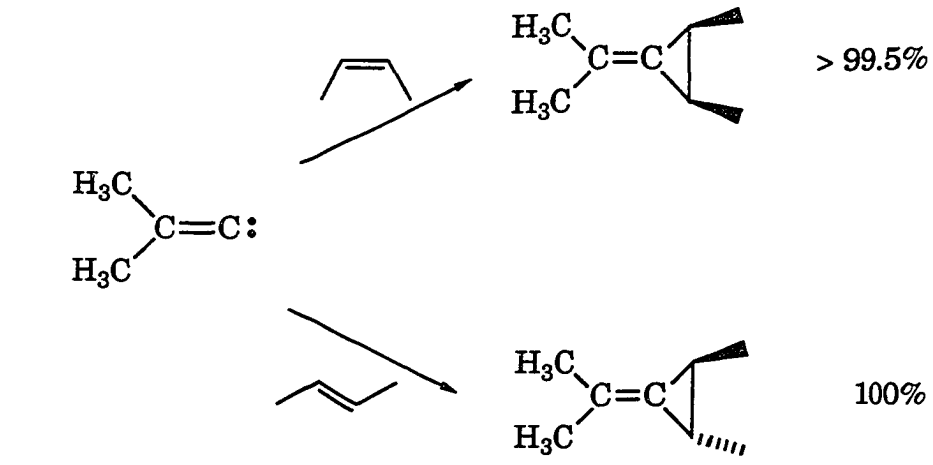
Of the three possible low energy states available to vinylidene, S_0 is predicted by *ab initio* calculation to be the lowest lying state.[3]



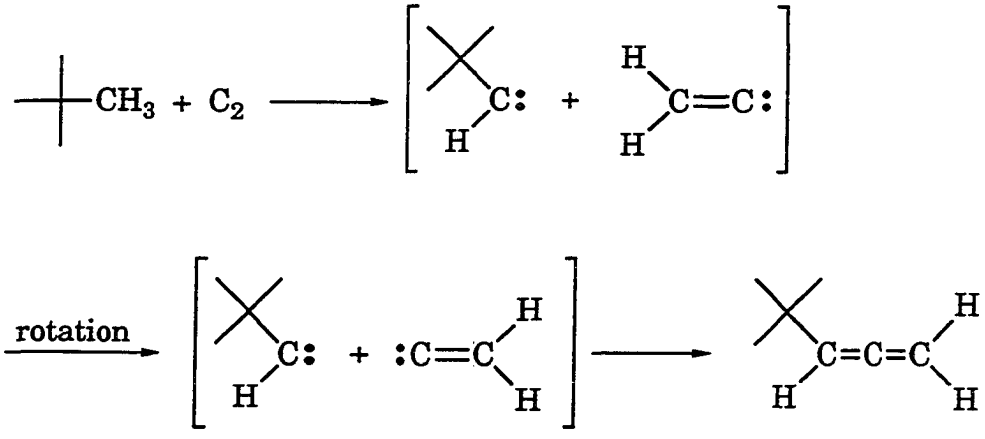
S_0 T_1 S_1

The singlet-triplet energy gap is calculated to be 42 kcal mol^{-1} and the excited state singlet an additional 13 kcal mol^{-1} higher.

While the short lifetime doesn't allow direct observation of vinylidene it has been experimentally demonstrated that the calculations are correct.[4] Using the Skell[5] technique it was demonstrated that isopropylidene reacts as a ground state singlet with butene. Addition of perfluorobutane does not effect the stereochemistry of the addition, thereby offering evidence that the triplet state does not lie below the singlet.



Scheme 4

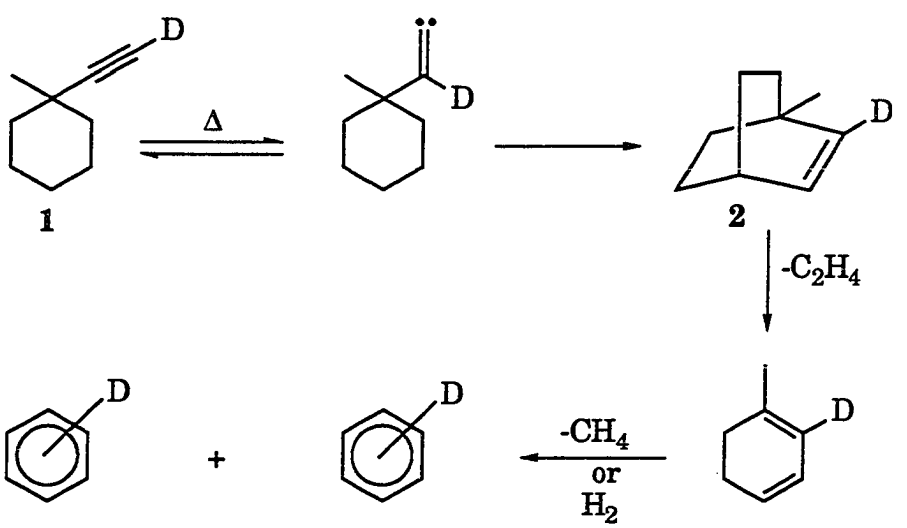


Scheme 5

Despite the short lifetime expected for vinylidene, Skell, Fagone, and Klabunde have proposed that, in the formation of *tert*-butylallene from neopentane and C_2,[6] vinylidene is able to rotate 180° and couple with *tert*-butyl carbene (Scheme 5).

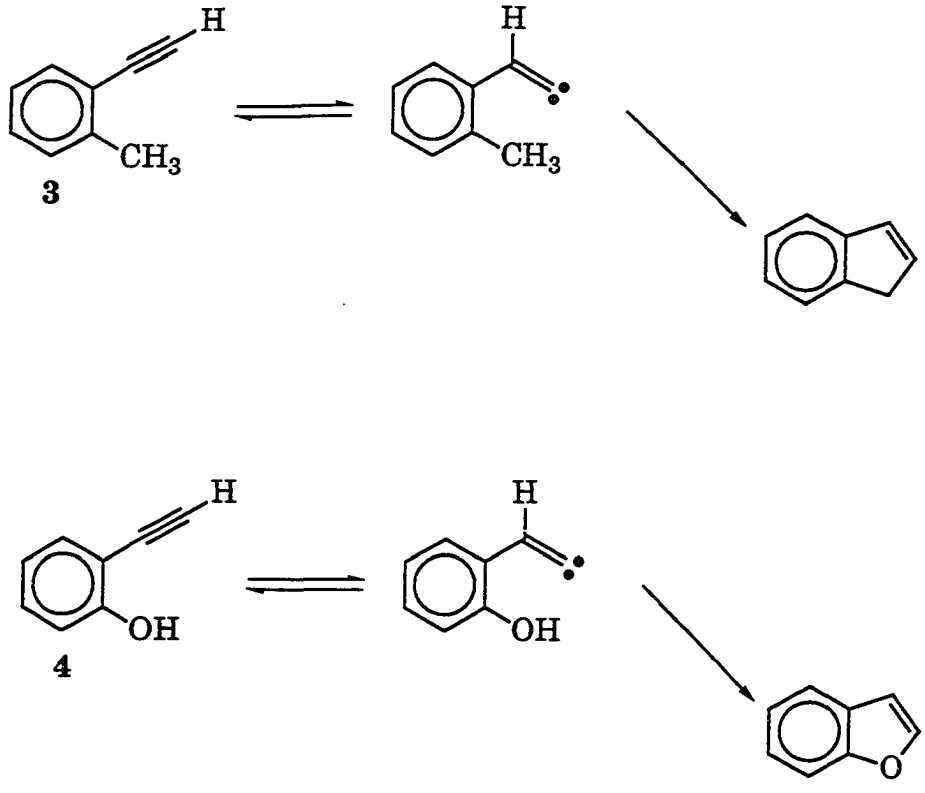
Mono alkyl and aryl substituted acetylenes have been shown to scramble in the fashion of unsubstituted acetylene.[7] Phenyl acetylene equilibrates completely at 700 °C while 1-adamantyl acetylene only scrambles 25% at 780 °C. *tert*-Butyl acetylene decomposes rather than scramble at 790 °C.[7]

Failure of *tert*-butyl acetylene and related compounds to scramble is attributed to the availablity of alternative reaction pathways involving vinylidenes. For example, monodeuterated toluene and benzene obtained in the pyrolysis of 1-methyl-1-(2-deuteroethynyl)cyclohexane **1** arise from the retro Diels-Alder reaction of the intermediate bicycle **2**[8] (Scheme 6).



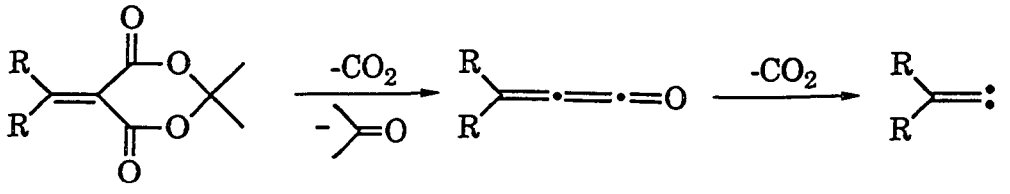
Scheme 6

Similar reactions are observed for aryl substituted vinylidenes. In an elegant study, Block and Orvanne have reported the pyrolysis of *o*-tolylacetylene **3** and *o*-ethynylphenol **4** produce indene and benzofuran, respectively (Scheme 7).[9]

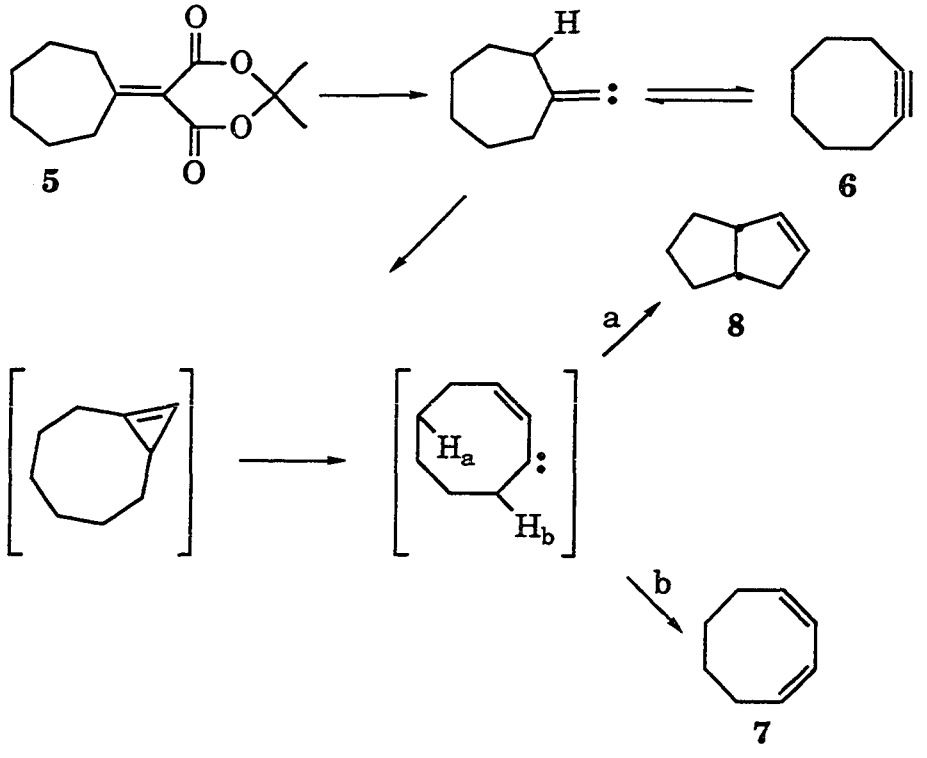


Scheme 7

Pyrolysis of Meldrum's acid derivatives of cyclic ketones results in a variety of rearrangements. The reaction procedes by extrusion of carbon dioxide and acetone from the isopropylidene malonate moiety the form a methylene ketene which then eliminates carbon monoxide to give a vinylidene (Scheme 8).[10]

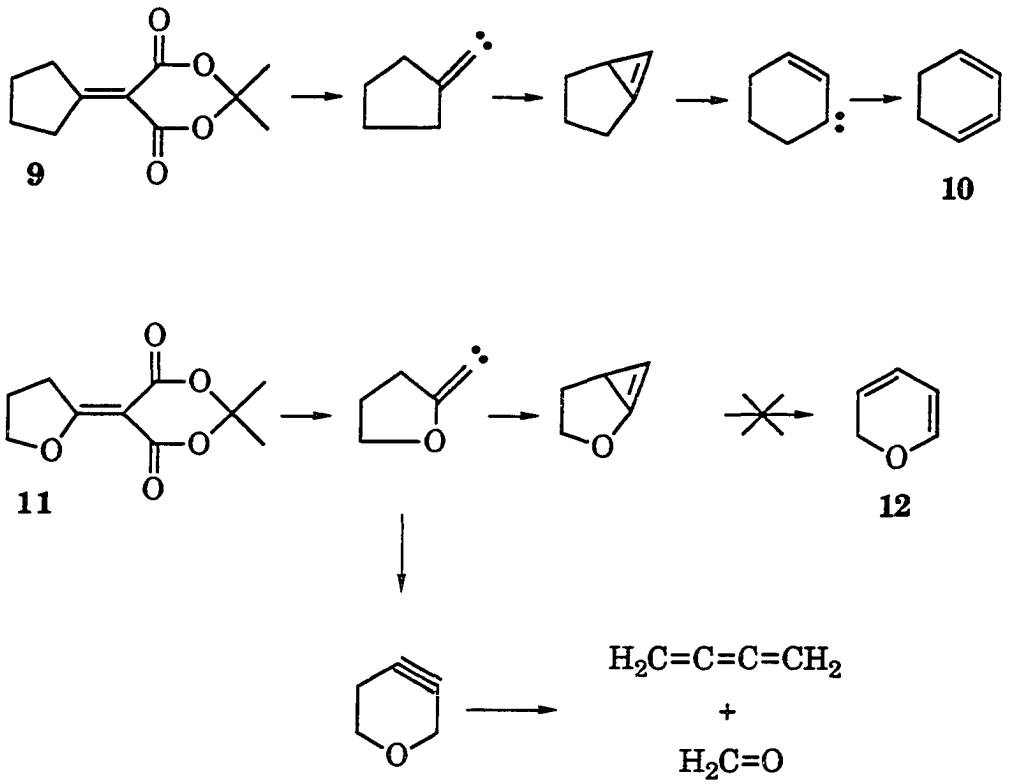


Scheme 8



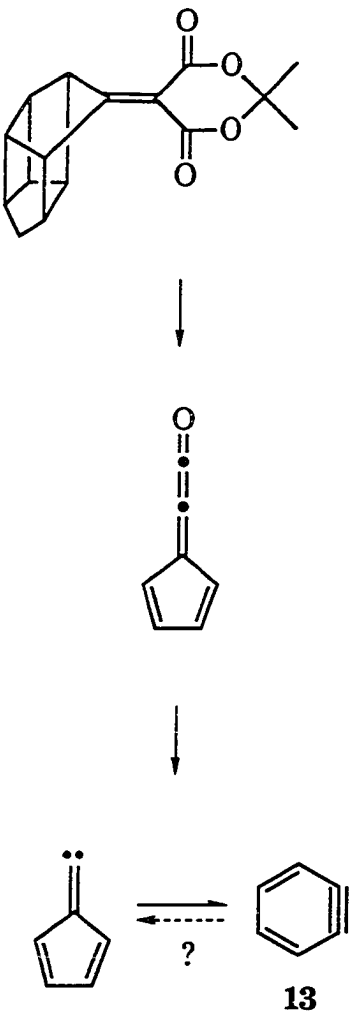
Scheme 9

In the case of the cycloheptanone derivative **5** both ring expansion to cyclooctyne **6** and γ-hydrogen insertion followed by rearrangement to cycloocta-1,3-diene **7** and bicyclo[3.3.0]oct-2-ene **8** are indicated (Scheme 9).[10] The ratios of expansion to insertion products is dependent on ring size.



Scheme 10

The cyclopentanone derivative **9** produces 1,3-cyclohexadiene **10** almost exclusively. But butatriene and formaldehyde are formed to the exclusion of 2H-pyran **12** in the heterocyclic analog **11**. This result was interpreted in terms of an intermediate ring expansion alkyne followed by a retro-Diels-Alder reaction (Scheme 10).[10]

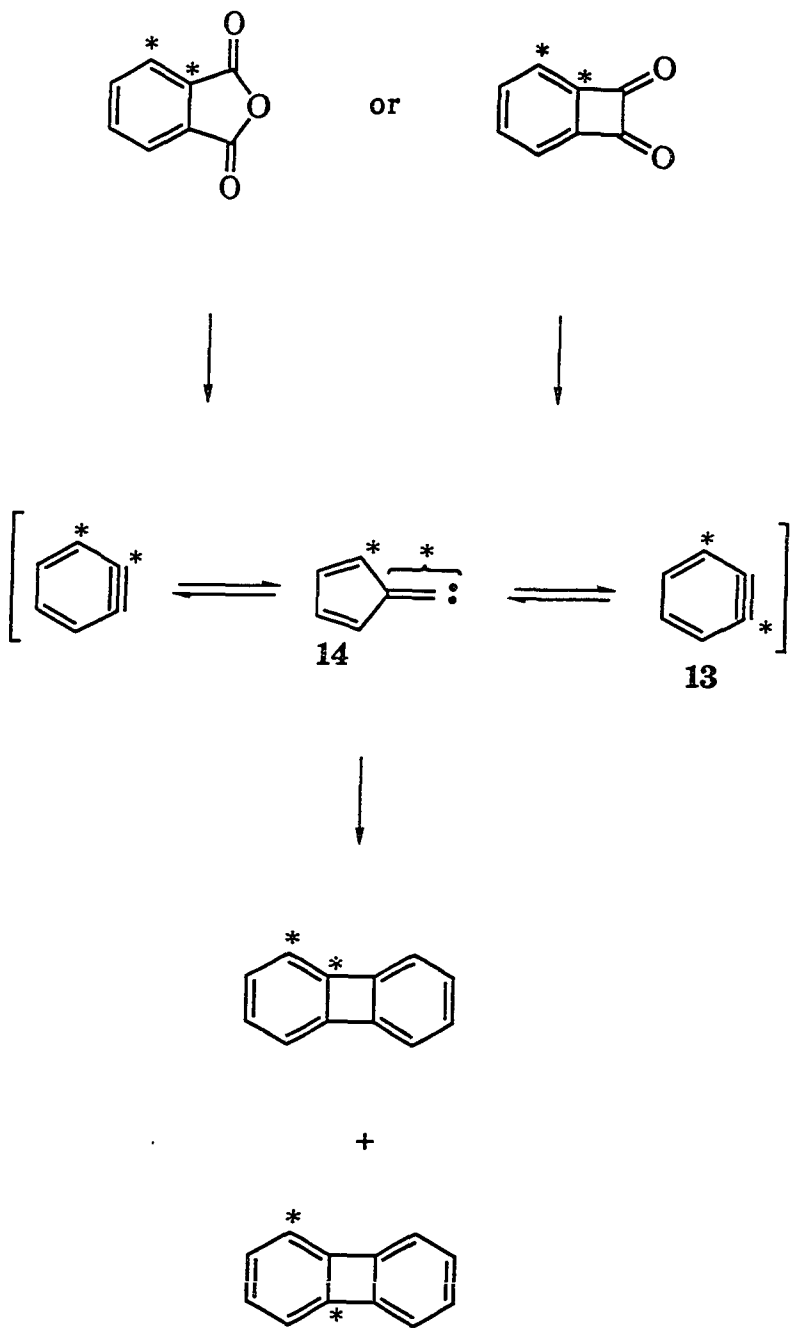


13

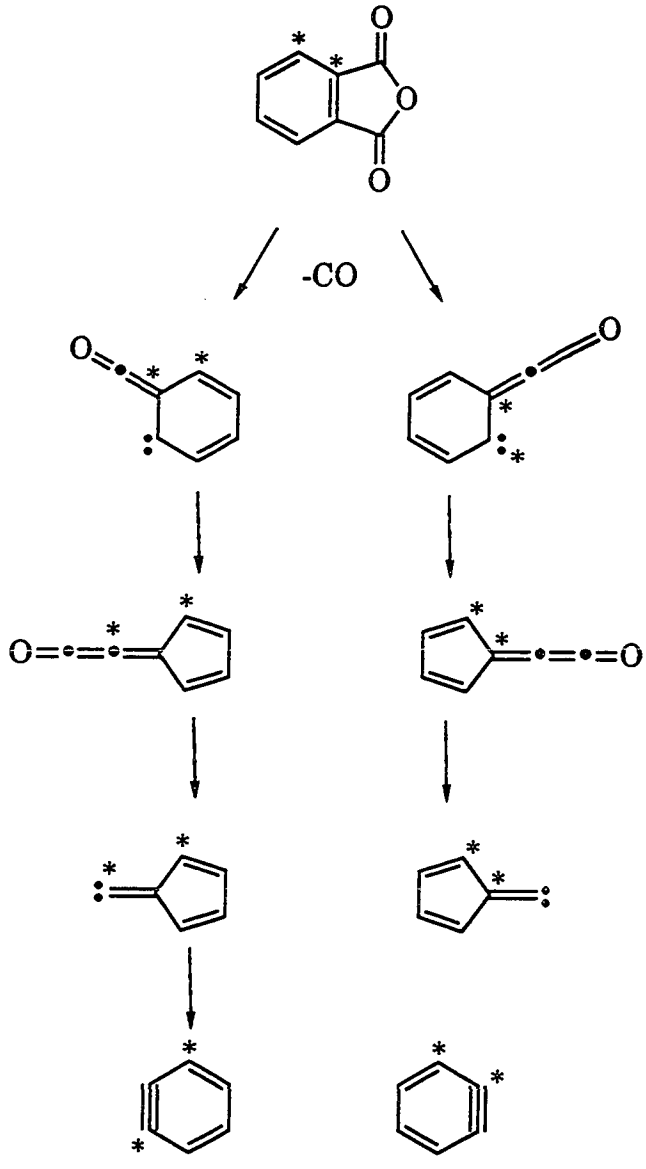
Scheme 11

This method has been applied to the synthesis of benzyne **13** (Scheme 11).[11]

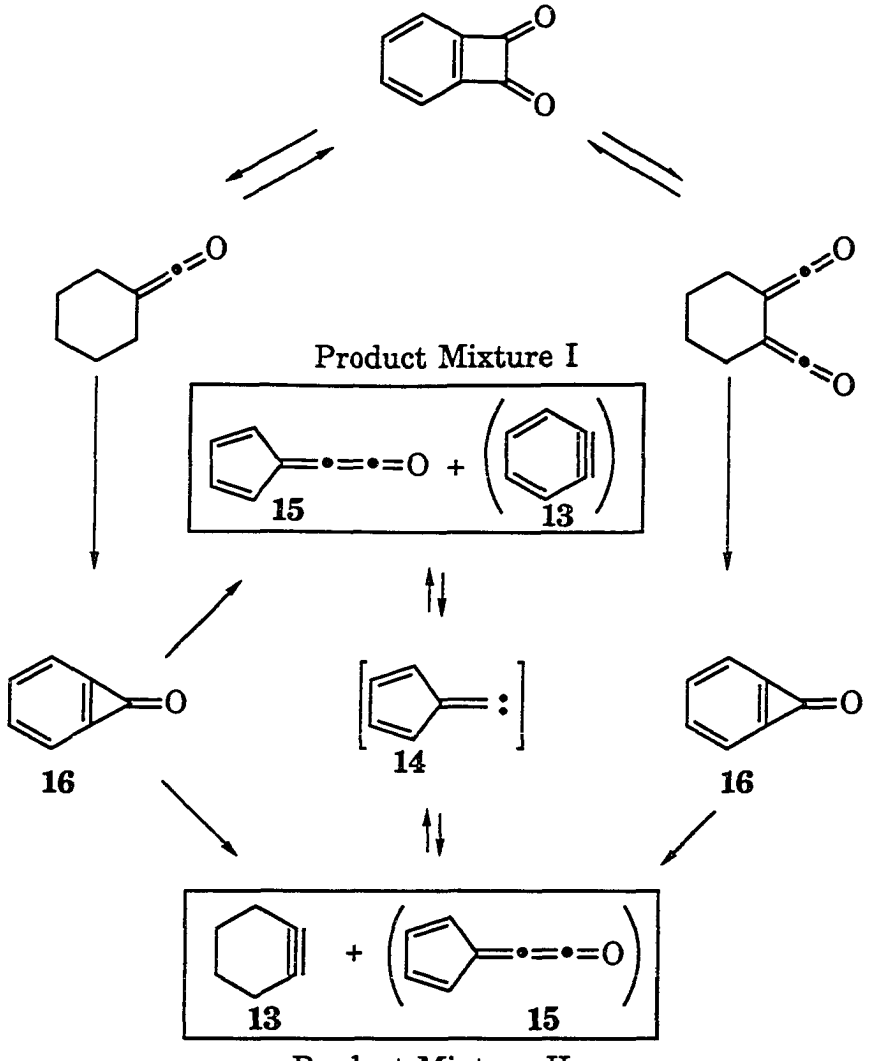
It was suggested that ^{13}C scrambling is evidence for the intermediacy of cyclopentadienylidenecarbene **14** (Scheme 12).[12] However, these results can be interpreted in terms of alternate mechanisms as in Scheme 13[11a] and Scheme 14.[13]



Scheme 12



Scheme 13

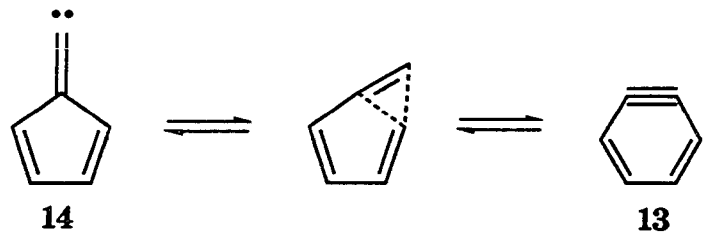


Scheme 14

The reaction shown in Scheme 14 was conducted in an argon matrix, thus CO is availabe to recombine with **13** or **14** to form **15** or **16**. Narrow band irradiation allowed formation of either of the product mixtures I and II by use of different wave length and, furthermore, allowed conversion of mixture I to

II and *visa versa*. Diffusion experiments, allowing migration of CO, implicate **14** as an intermediate in the transformation of **13** to **15**.

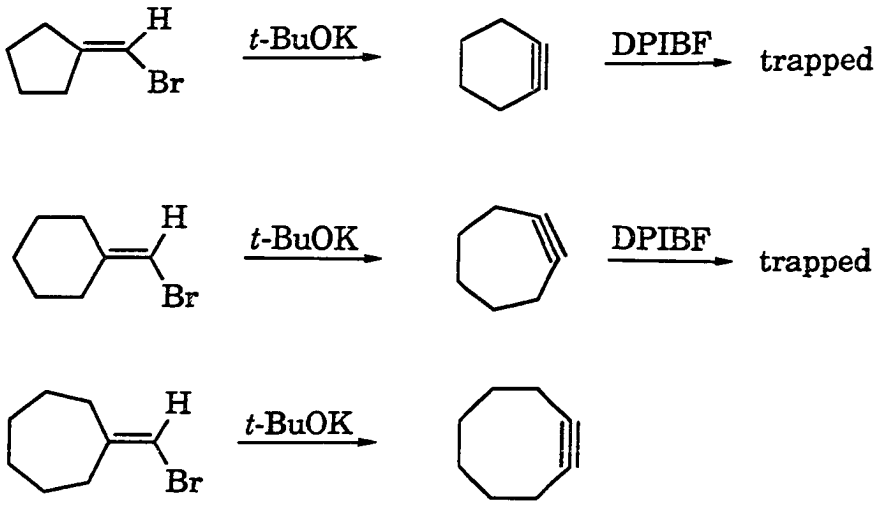
Ab initio calculation studies by Burton and coworkers suggest cyclopentadienylidenecarbene **14** is transformed to benzyne **13** (and *visa versa*) via the transition state indicated in Scheme 15.[14] Benzyne was found to be 43 kcal mol^{-1} more stable than the vinylidene **14** and the transformation barrier to be only 4.5 kcal mol^{-1}.



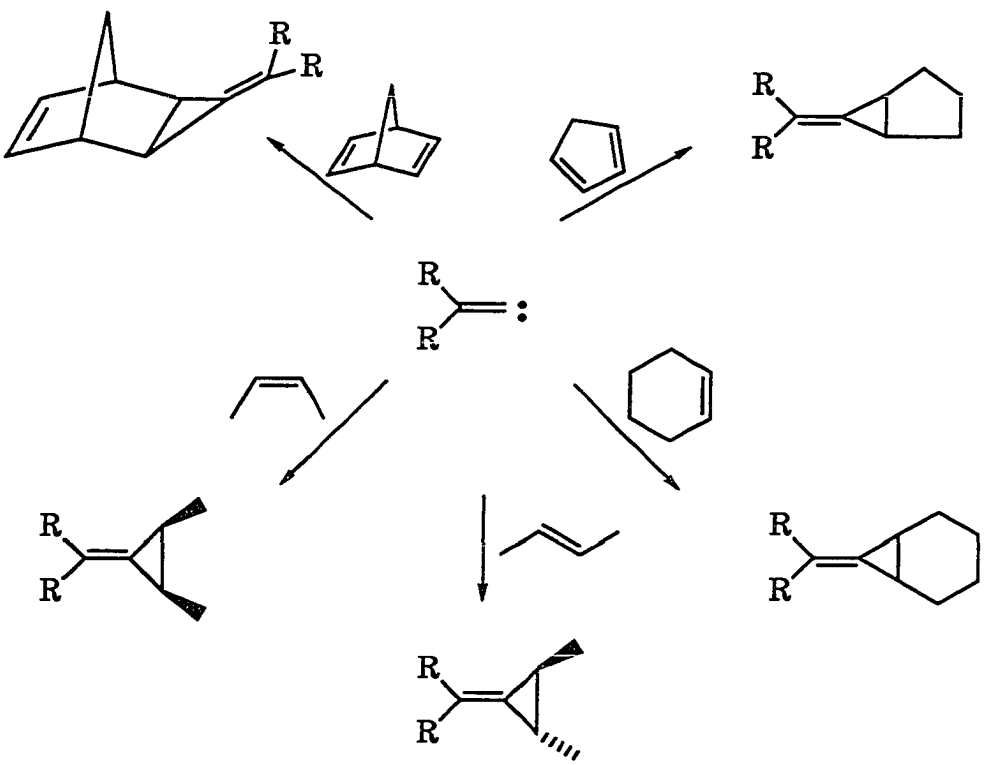
14 **13**

Scheme 15

In solution substituted vinylidenes typically undergo ring expansions to cycloalkynes which can be trapped by diphenylisobenzofuran (DPIBF) or isolated (Scheme 16), or in the presence of alkenes intermediates can be trapped (Scheme 17).[16]



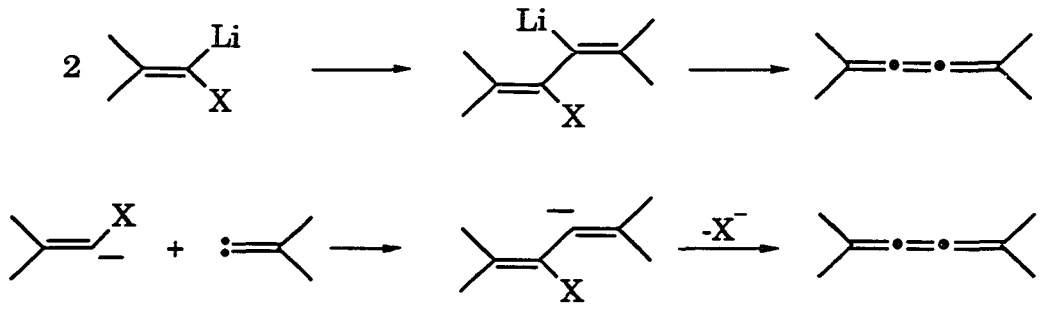
Scheme 16



Scheme 17

Dimerization forming butatrienes are best viewed in terms of stepwise mechanisms (Scheme 18).[17]

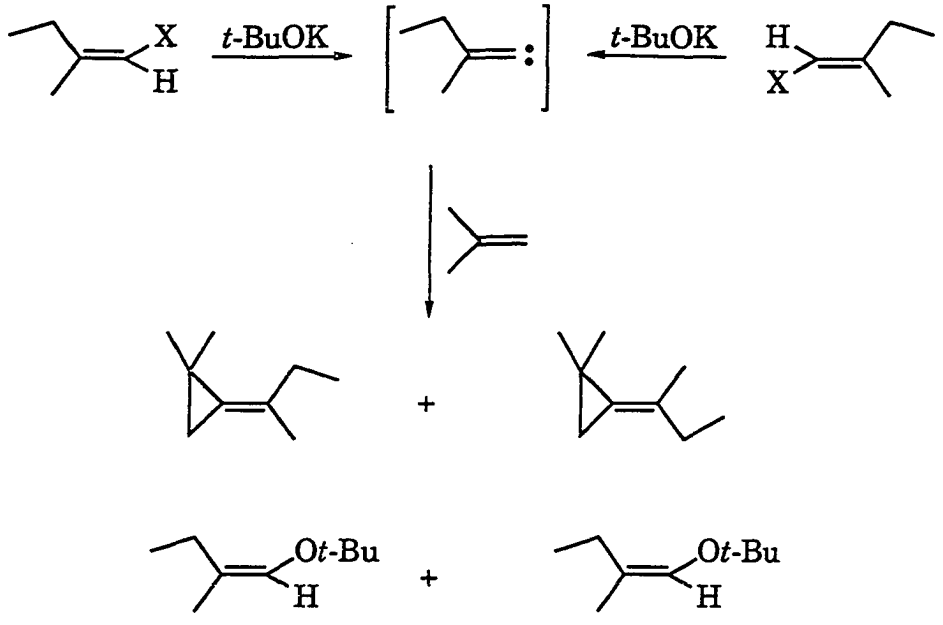
This underscores the importance of the degree of encumberance of vinylidenes. Just as with carbenes, three major species should be considered: 1) organometallic reagents 2) methylene carbenoids, and 3) free methylene carbenes.[18]



Scheme 18

Organometallic reagents typically give anionic or radical reactions as in Scheme 18. Free vinylidenes typically undergo insertions or rearrangements. Carbenoids generally react much like free carbenes but, depending on the degree of association with the leaving group, can give organometallics like results. Carbenic character can be increased by higher temperatures, use of better leaving groups or addition of a metal complexing agent.

The degree of association of a carbene with a leaving group is reflected in the stereoselectivity of addition of an asymmetric vinylidene to an asymmetric olefin. If a pair of isomeric vinylidene generators give the same product mixtures when allowed to react with a substituted alkene, a "free" vinylidene is indicated (Scheme 19).[18]

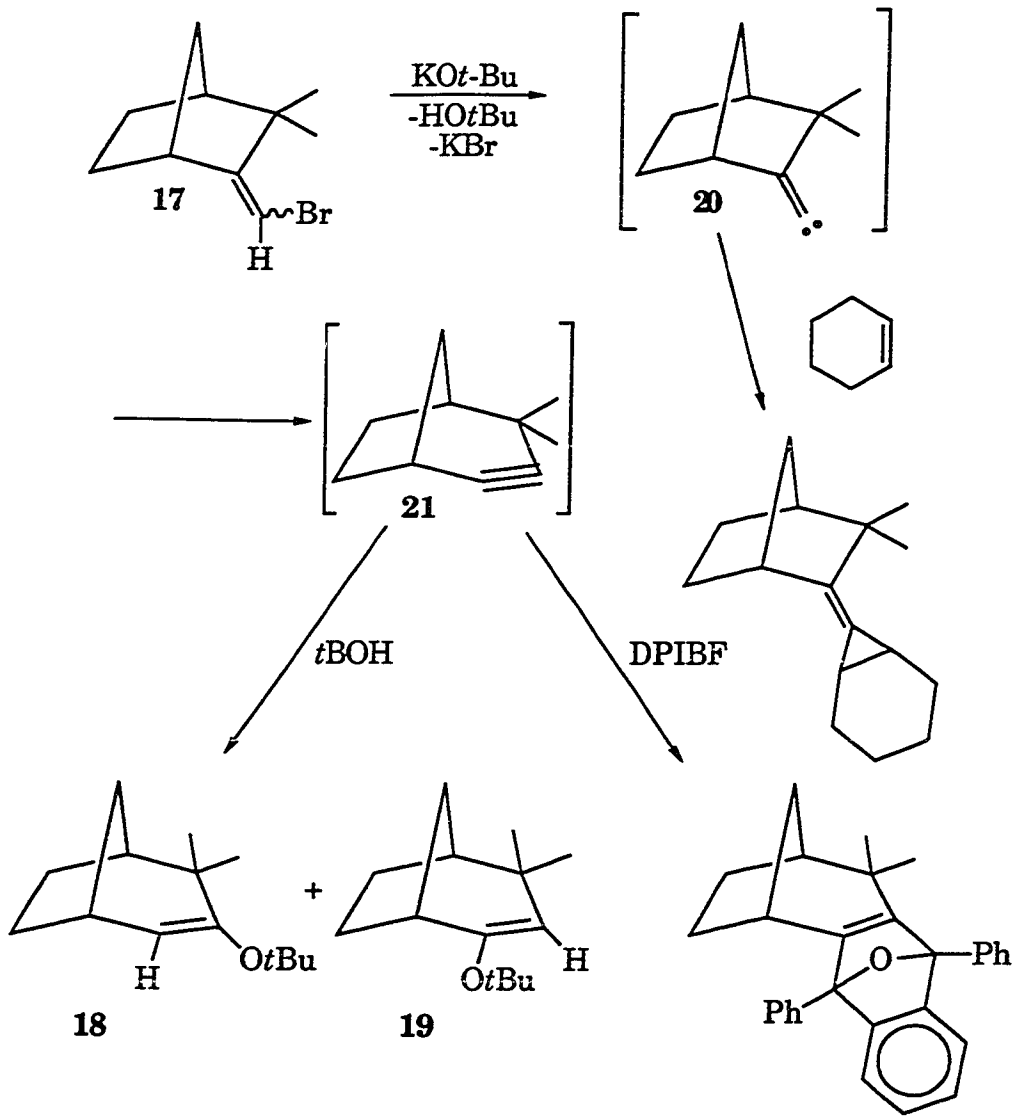


Scheme 19

While the study of cyloalkylidenes has received much attention reports dealing with their bicyclic counterparts have been fairly sparse. Those that have appeared have revealed intriguing behavior.

Substituted norbornyl systems have been studied by Erickson and Wolinsky[19] and by Mehta.[20] Both cases are believed to involve ring enlargement to a transient bicyclic alkyne produce from the bicyclic alkylidene.

In the study of Erickson and Wolinsky[19] it was demonstrated that α-bromocamphene **17** treated with potassium *tert*-butoxide in toluene at 100 °C

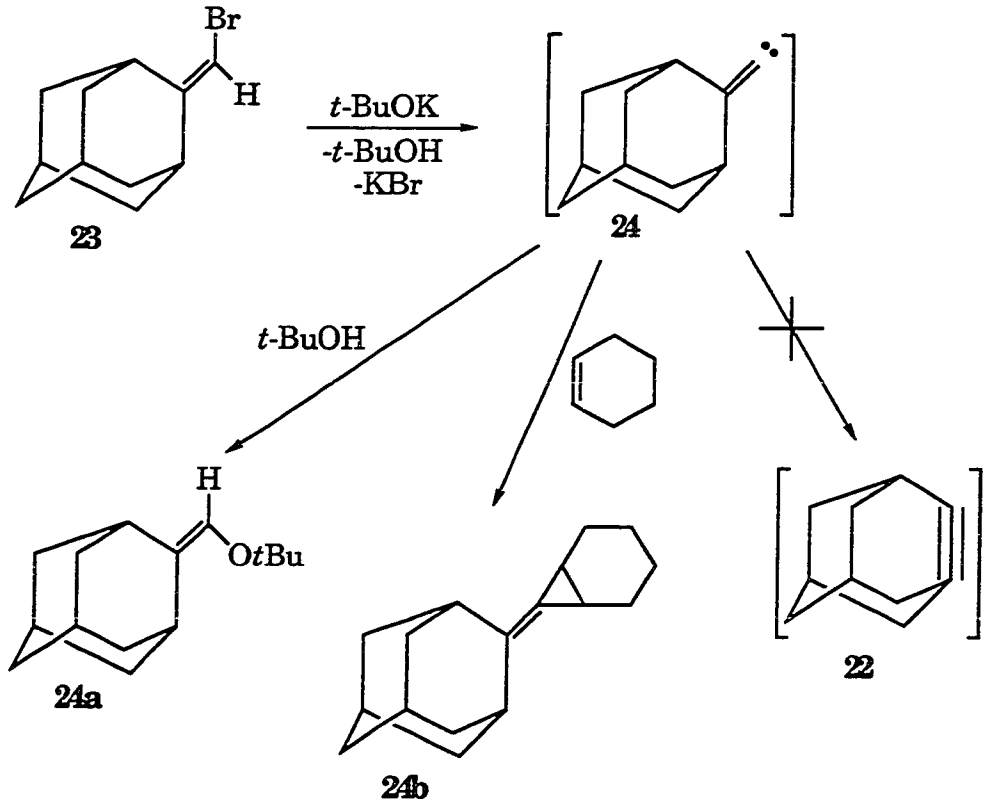


Scheme 20

produces the isomeric *tert*-butyl ethers **18** and **19** (Scheme 20). This was interpreted to indicate formation of a carbene **20** which then rearranged to the alkyne **21** and was trapped by the *tert*-butanol formed in the generation of the vinylidene. The intermediacy of the vinylidene and alkyne were confirmed by trapping with cyclohexene and diphenylisobenzofuran, respectively.

Mehta[20] reported the trapping of the analogous ring expanded product arising from the treatment of ω-bromolongifolene with potassium *tert*-butoxide. Apparently, no attempt was made to trap the vinylidene.

The adamantyl analog of the camphenyl systems, on the other hand, appears to be resistant to such ring expansion. Sasahi and coworkers[21] found no evidence for ring expansion to homoadamantyne **22** when ω-bromo-



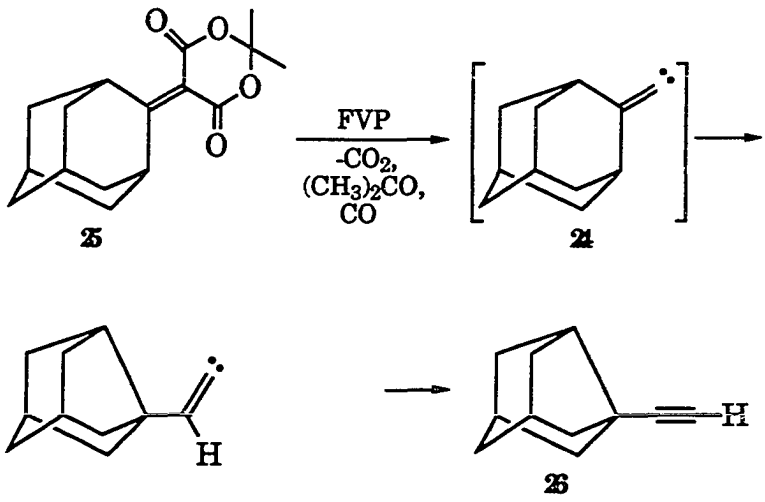
Scheme 21

methylene adamantane **23** was treated with potassium *tert*-butoxide in toluene. The existence of the transient vinylidene **23** was confirmed by cyclohexene trapping and by *tert*-butyl ether formed by reaction with the *tert*-butanol formed in the reaction (Scheme 21).

The adamantylidene carbene **24** was also produced by base-induced decomposition of 2-hydroxy-2-[*N*-nitroso-*N*-acetylamino)methyl]-adamantane, and by thermal decomposition of [(tosylazo)methylene]adamantane. Additionally, 18-crown-6 ether was employed in the dehydrobromination experiments to ensure formation of "free" carbene rather than the carbenoid.[22]

Failure of the ring to expand was attributed "to a considerable strain increase in the ring enlargement of [the vinylidene] to [the alkyne] due to the rigidity of molecular framework." Further, it was noted that 4-homoadamantenyl-4-triflate cleanly ring contracts to (ω-triflatemethylene)adamantane.[23]

A peculiar alkylidene carbene reaction was reported by Scharp and Wiersum[24] involving a ring contraction following formation of the vinylidene **24** by pyrolysis of the Meldrum's acid derivative of adamantanone **25**. Flash vacuum pyrolysis at 600 °C gave an 81% yield of 3-noradamantylacetylene **26** (Scheme 22).



Scheme 22

RESULTS AND DISCUSSION

The ring expansion of the [2.2.1]alkylidenecarbene **20** would appear to be an energetically similar (if not less favorable) process to the ring expansion of adamantylidene carbene **23**. Yet, in the [2.2.1] case the ring expansion is facile[19,20] and in the adamantyl case ring expansion isn't observed.[21,23,24] Molecular mechanics appears to be a reasonable means of evaluating the strain of the frameworks in question.

The MMX program[25] was used to evaluate the adamantyl to homoadamantyl problem and the [2.2.1] to [3.2.1] problem. In addition, a series of similarly sized cyclic systems which have been demonstrated to ring expand were evaluated.

Since the program is not parameterized to handle the vinylidene the corresponding methylene systems were calculated. This should have negligible effect on the strain of the system, and, furthermore, any effect should be approximately equal in each system, therefore, allowing a reasonable comparison. Effort was made to find the minimum energy conformation in each case. This is fairly simple for the cage systems and small cyclic systems but becomes more difficult with increased ring size.

Table I summarizes the results of the calculations. Two sets of energies are given for each system. The first is the total strain of the system. The second, parenthetically enclosed set is the unsaturation strain (US) of the system determined by subtracting the strain of the saturated system from that of the unsaturated system in the fashion suggested by Lesko and Turner[26] for Bredt olefin comparison.

Table I. Strain energies of *exo*-methylenes and alkynes

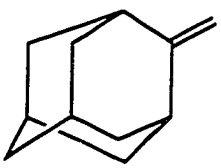
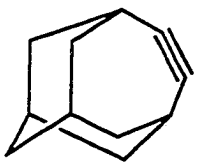
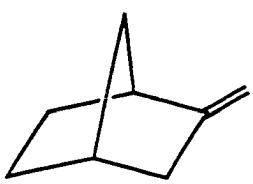
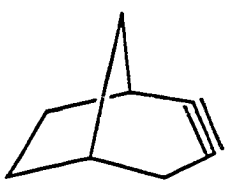
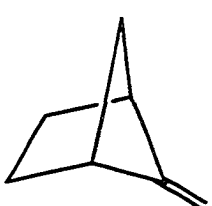
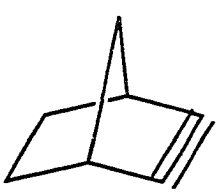
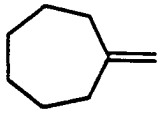
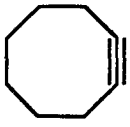
total strain (kcal mol^{-1}) (unsaturation strain (kcal mol^{-1}))		difference (kcal mol^{-1}) (alkyne-methylene)
		
17.46 (-2.07)	40.97 (12.96)	23.51 (15.03)
		
23.56 (0.67)	45.72 (26.45)	22.16 (25.78)
		
49.16 (3.58)	94.87 (71.78)	45.71 (68.20)

Table I. continued

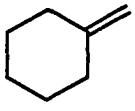


12.87
(-2.13)

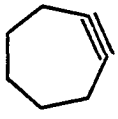


18.45
(-0.96)

5.58
(1.17)

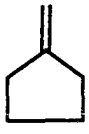


6.04
(0.75)

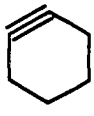


20.39
(6.08)

14.35
(5.33)



10.80
(-0.81)

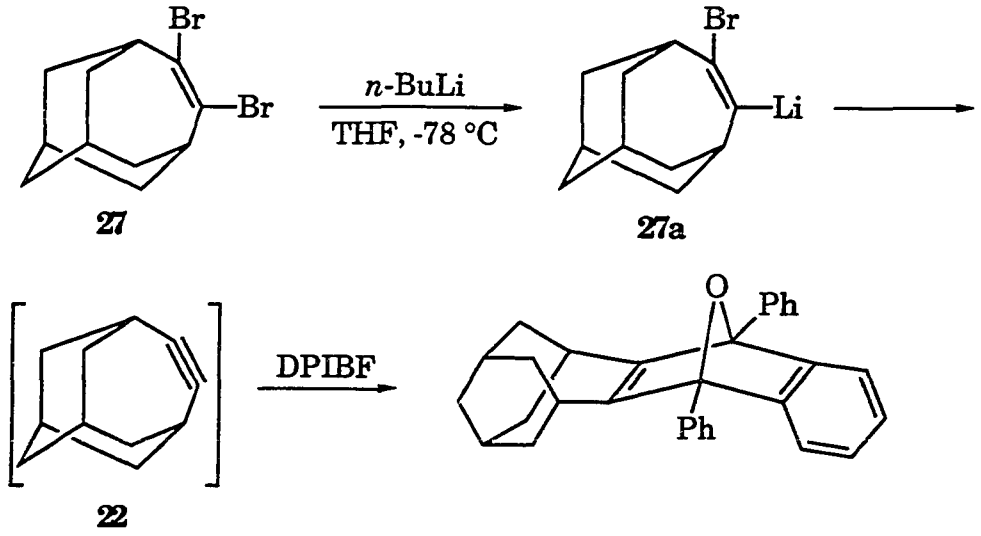


30.80
(24.25)

20.00
(24.25)

The results of the cyclic systems show the trend one might intuitively expect, and which is reflected in both gas phase and solution studies. The seven-membered ring system cleanly expands to isolable cyclooctyne. The more strained five- and six-membered ring systems give ring expanded alkynes but competing side reactions occur.

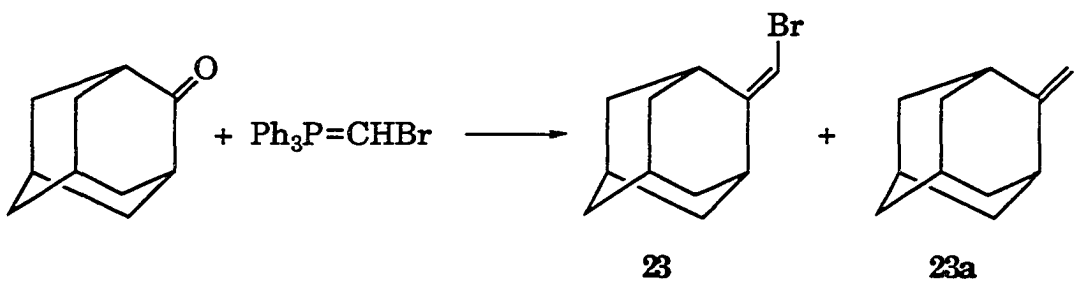
The strain in the bicyclic systems seem to follow the trend of the cyclic systems nicely. Overall energies are greater due to the greater strain inherent in the bicycles, however the change in strain is reasonable considering that the alkyne is now in two rings rather than one.



Scheme 23

The similarity of the energies of the larger bicycles, coupled with a recent report of diphenylisobenzofuran (DPIBF) trapping of homoadamantyne **23**[27] produced by base induced elimination from dibromohomoadamantene **27** (Scheme 23) prompted reinvestigation of the results of Sasaki and coworkers.[21] By analogy to the homoadamantenyl triflate study[23] (*vide supra*), if strain were responsible for the contraction, the lithiated bicycle **27a** should have undergone a similar rearrangement.

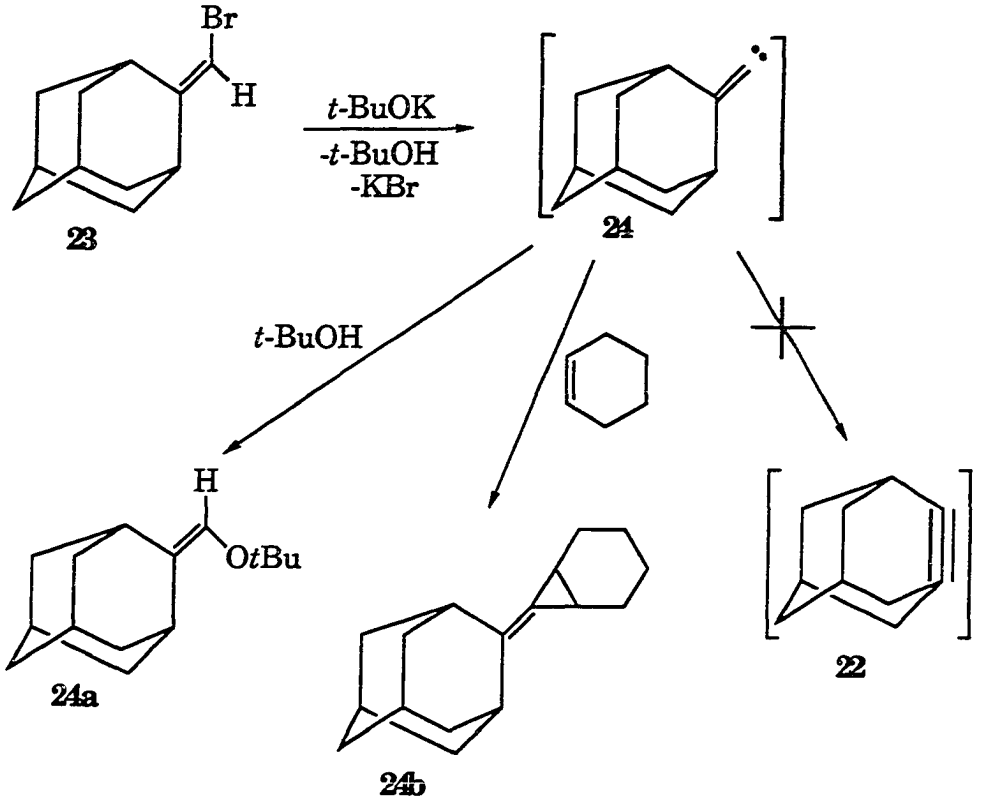
(ω-Bromomethylene)adamantane **23** was prepared by the reaction as described by Sasaki,[21] with slight modification, in 21% yield. Non-brominated methyleneadamantane **23a** was present in the reaction mixture (Scheme 23A). The products **23** and **23a** were isolated by preparative GC.



23 **23a**

Scheme 23A

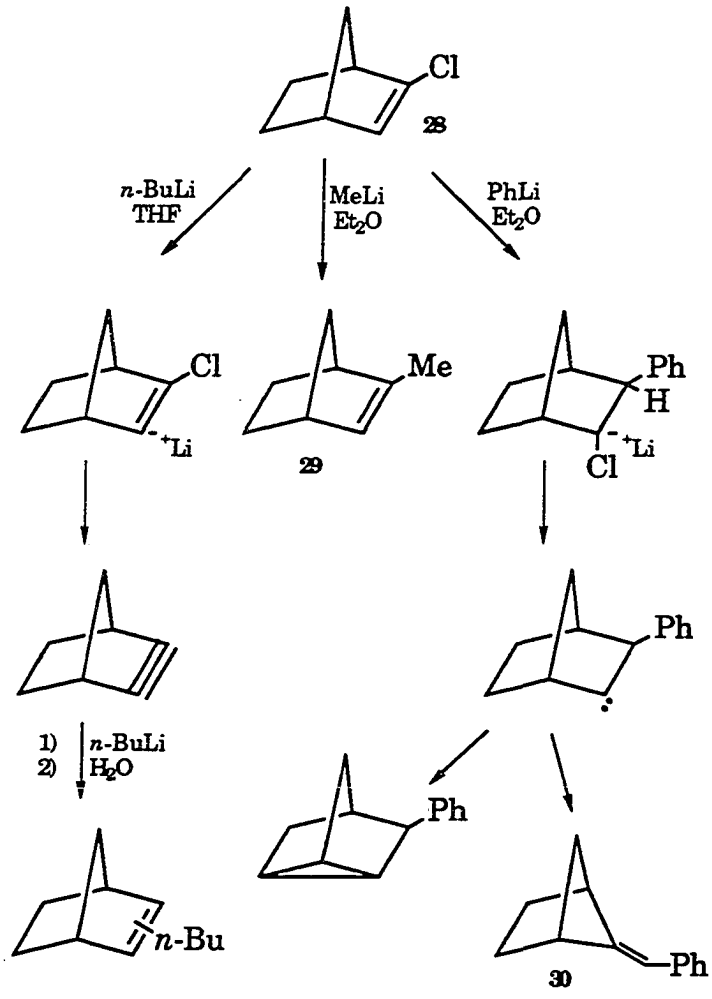
The bromide **23** was treated with potasssium *tert*-butoxide as described by Wolinsky.[19] It was hoped that in the absence of the crown ether used by Sasaki and coworkers,[21] the vinylidene **24** would ring expand and the resulting alkyne **22** could be trapped as described by Koichi et al.[27] In the presence of cyclohexene both the *tert*-butyl alcohol adduct **24a** and the cyclohexene adduct **24b** were observed. In the presence of DPIBF no alkyne trapping was observed (Scheme 23B).



Scheme 23B

While the experimental results are disappointing, the calculated results argue against ring strain being the major factor in the vinylidene-acetylene rearrangement.

Working from the direction of acetylene to vinylidene, the difference in results between the bromide and triflate in the homoadamantyl case point to rolls of leaving groups, ion pairs, or solvent as the key elements in determing the selectivity of the reaction. This is clearly demonstrated by the work of Gassman and coworkers.[28]

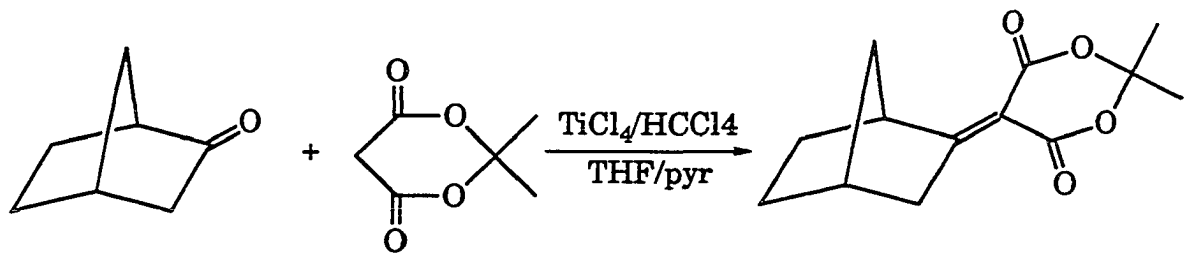


Scheme 24

Gassman et al reported that 2-chloronorbornene **28** was transformed to 2-methylnorbornene **29** with retention of stereochemistry upon treatment with methyl lithium. Next, Gassman and Atkins reported that treatment of **28** with phenyl lithium gives 5-benzalbicyclo[2.1.1]hexane **30**. This reaction is reported to be very sensitive to solvent and phenyl lithium purity; purer solvent gives less **30**. Finally, Gassman and Valcho demonstrated loss of stereochemistry when **28** is treated with *n*-butyl lithium (All in Scheme 24).

The methodology used by Scharp and Wiersum[24] in the adamantyl study (*vide supra*) seemed to offer hope of examining the effect of ring strain on alkylidene rearrangement without complications arising from salt and solvent.

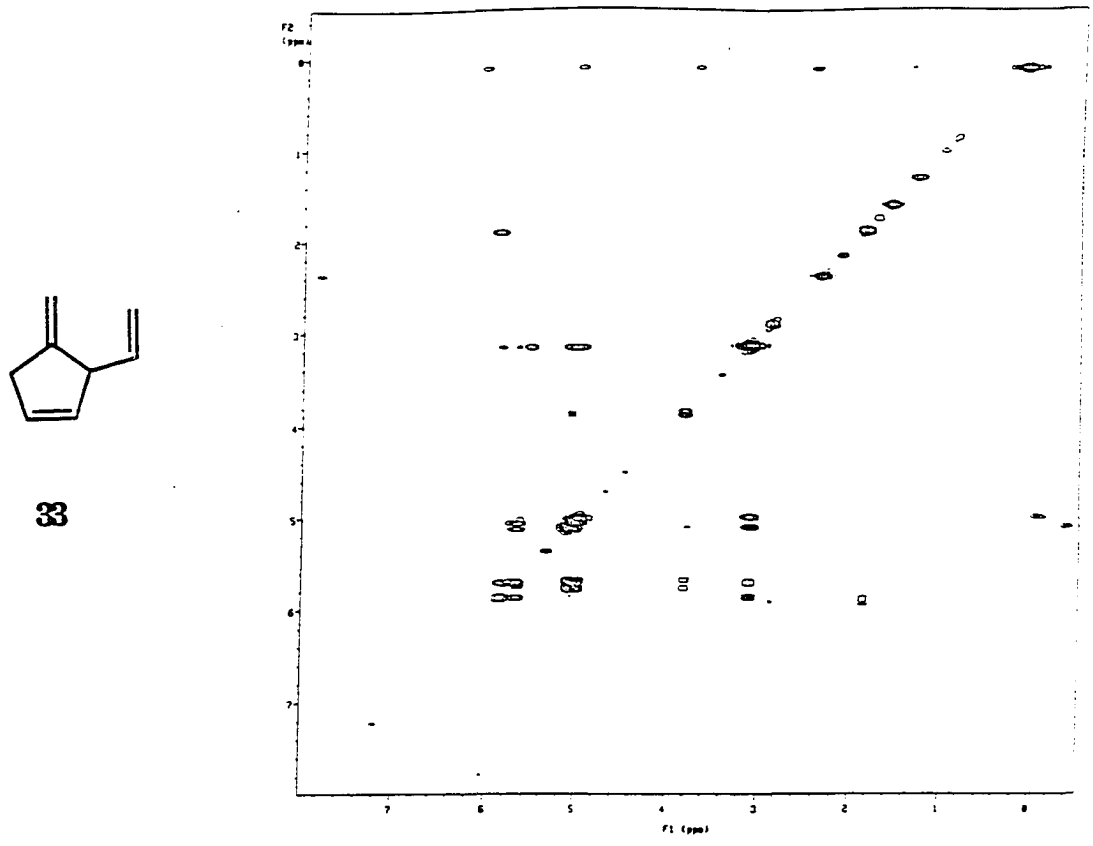
Using Brown's method[29] for the formation of Meldrum's acid derivatives of ketones, norcamphor **30** was condensed with 2,2-dimethyl-1,3-dioxane-4,6-dione **31** in 42% yield. The product **32** was easily purified by column chromatography.



30 **31** **32**

Scheme 25

Precursor **32** was subjected to flash vacuum pyrolysis. Besides acetone, carbon dioxide, and carbon monoxide, three principle components of the pyrolysate (ca. 15% of the mixture) were separated and isolated by preparative gas chromatography. Mass spectra revealed isomeric hydrocarbons of the formula C_8H_{10}, correct mass for the vinylidene generated. Infrared spectra revealed only the presence of olefinic carbons and hydrogens in all three hydrocarbons and in the case of **34** an acetylenic stretch was present.

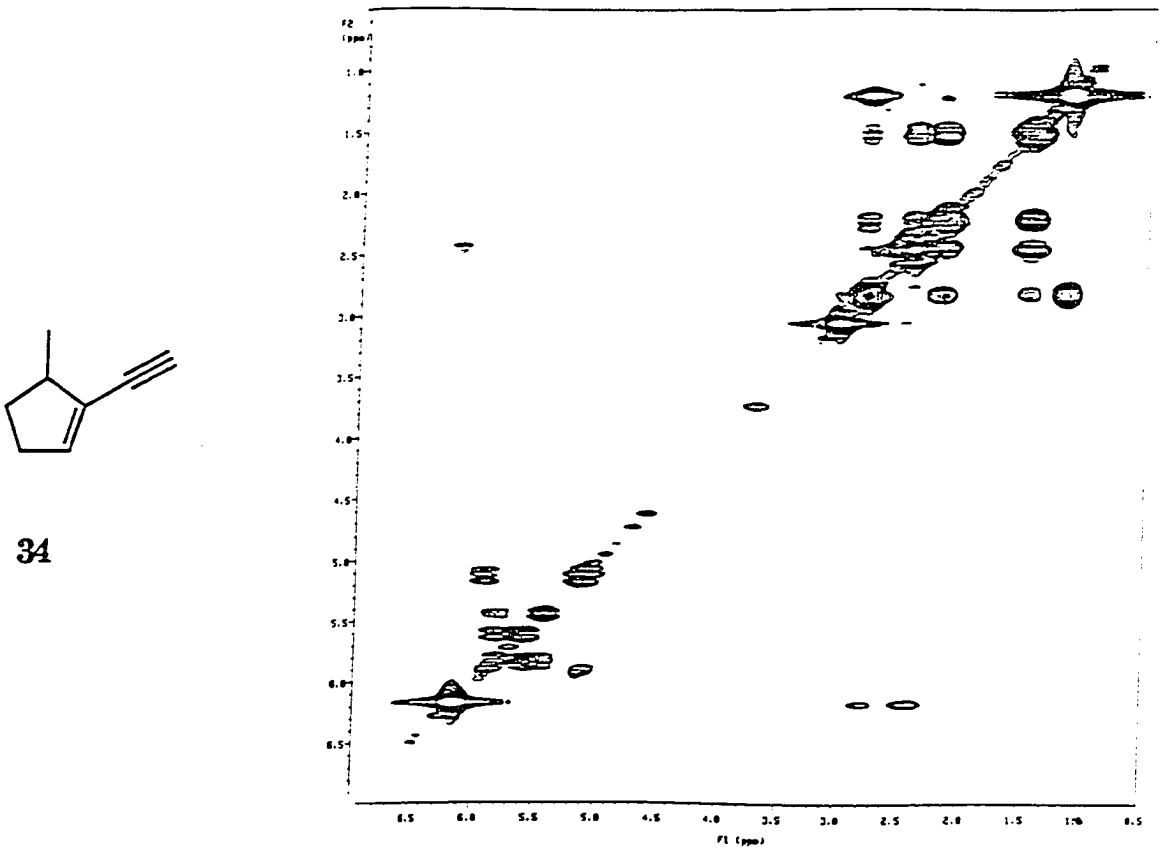


33

Figure 1. COSY spectrum for 4-methylene-3-vinyl-cyclopentene **33**.

Because five of the seven vinyl protons of hydrocarbon **33** absorb in a narrow region between 4.9 and 5.1 ppm, the ^{1}H NMR spectrum wasn't useful for connectivity. The three aliphatic protons were shifted far down field.

Both gated decoupled and ^{1}H coupled ^{13}C NMR spectra were acquired. A non-protonated carbon at 152 ppm was suggestive of an exocyclic methylene.[47] Of the remaining five olefinic carbons two are doubly protonated and three are



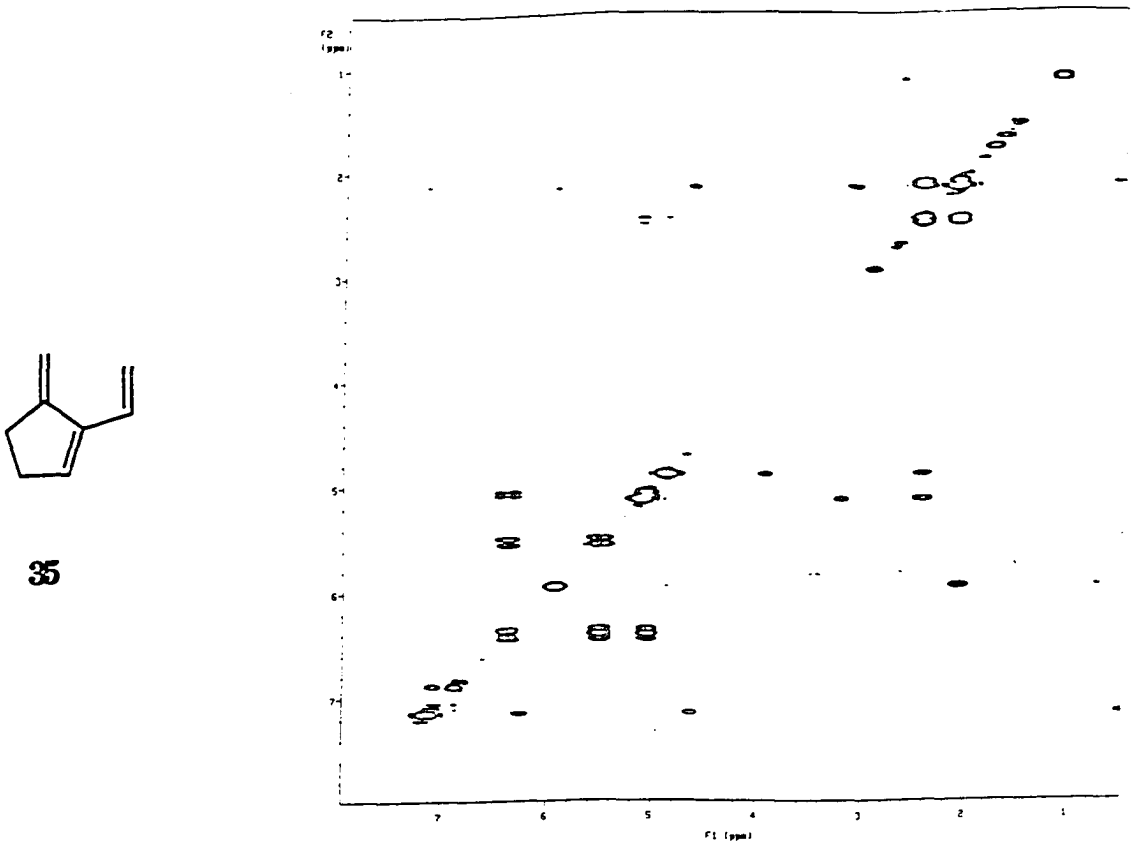
34

Figure 2. COSY spectrum for 3-methyl-2-ethynyl-cyclopentene 34.

singly protonated. This leads to consideration of three vinyl substituted methylenecyclpentenes.

The COSY spectrum shows that the aliphatic protons are not coupled, thus excluding all but one structure, 4-methylene-3-vinylcyclopentene 33.

Again, both gated-decoupled and ^{1}H coupled ^{13}C were acquired for hydrocarbon **34**. The presence of a terminal acetylene was apparent. Only one



35

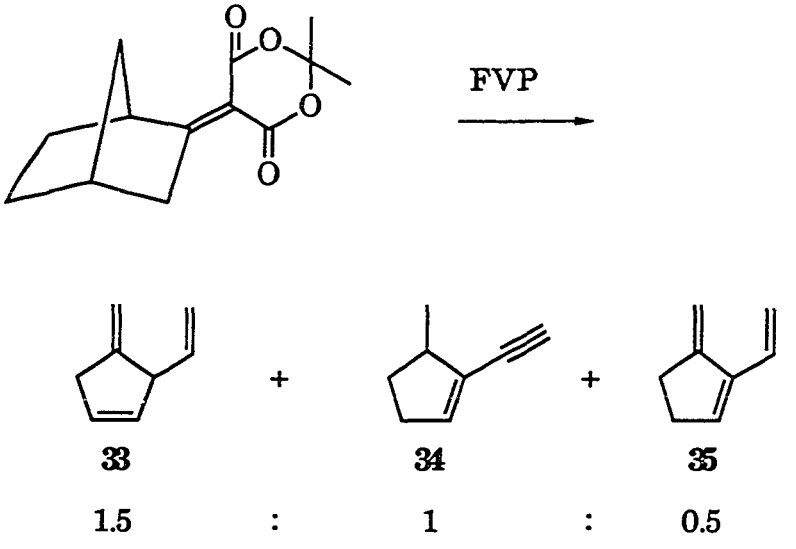
Figure 3. COSY spectrum for 3-methylene-2-vinyl-cyclopentene 35.

of the two olefinic carbons was protonated. The aliphatic region of the spectrum showed one trisubstituted carbon, two disubstituted carbons, and a methyl. This leads to several methyl-, ethynyl-substituted cyclopentenes, all but three of which are eliminated because the methyl protons are split by a single proton.

The COSY spectrum allows elimination of all but one structure because the methylenes are strongly coupled. Further, assignment of all but the methylene proton is possible.

The ^{1}H NMR spectrum for **35** shows 6 unique vinyl protons. Coupling was indiscernable because of impurities.

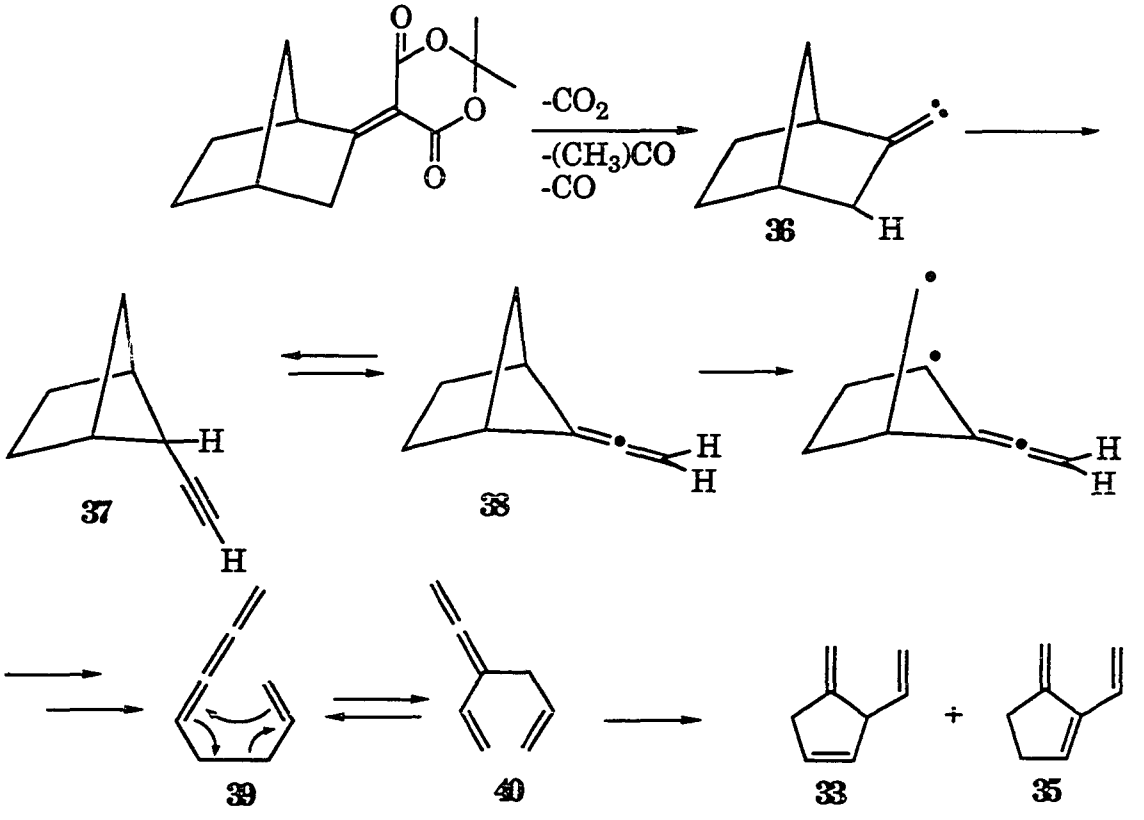
^{13}C NMR data revealed six olefinic carbons, two each with two, one, and no hydrogens attached. Again, the peak at 150.9 indicated an exocyclic double bond.[47] Both aliphatic carbons are diprotonated. This reduced likely structures to three methylene-vinylcyclopentenes.



Scheme 26

The COSY spectrum shows strong coupling between the aliphatic protons and also between one vinyl proton and a pair of aliphatic protons. This leaves only one structure for **35** 3-methylene-2-vinylcyclopentene. This conclusion is in excellent agreement with the structure published by Priebe and Hopf.[31]

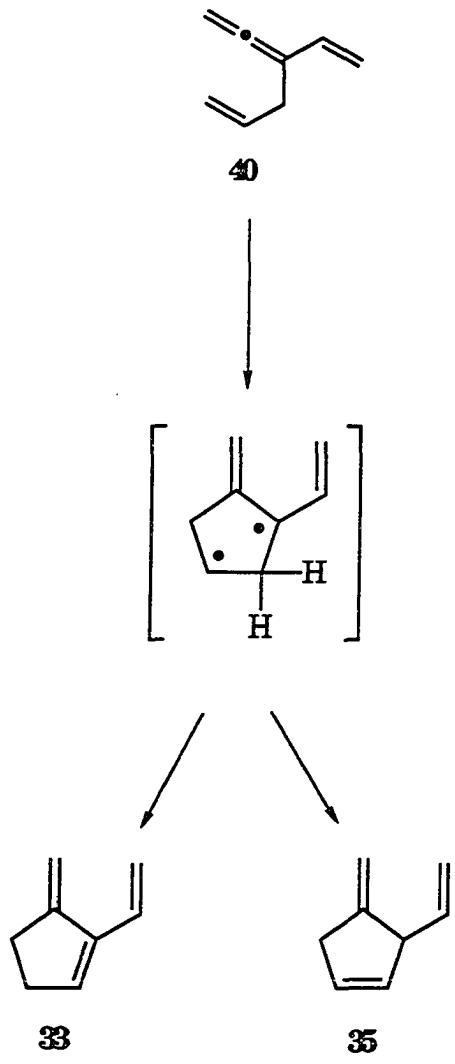
The mechanistic rationale for the products formed (Scheme 27) begins with formation of the alkylidene carbene **36**. Ring contraction, analogous to that reported by Scharp and Wiersum,[24] gives acetylene **37** followed by acetylene-allene isomerization to give **38**.



Scheme 27

Roth reported the ring opening of 4-methylene bicyclo[2.1.1]hexane to the linear ene-allene.[30] Similar ring openeing of **38** gives the ene-cumulene **39** which can then undergo a Cope rearrangement to give **40**.

Priebe and Hopf[31] reported the thermal isomerization of **40** to give a mixture of **33** and **35** (Scheme 28).

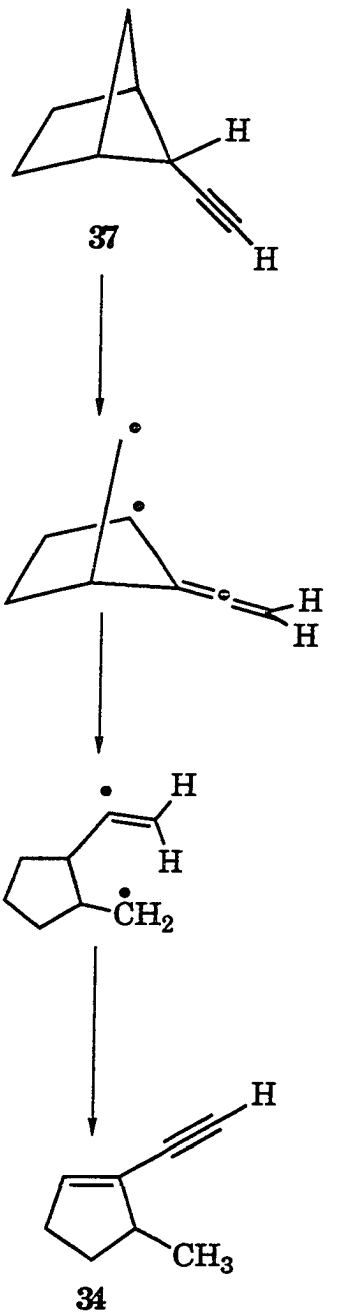


40

33 35

Scheme 28

A hydrogen migration from C-6 to C-8 of **37** would give rise to **34**. This can be rationalized in terms of a ring cleavage followed by a hydrogen abstraction in which case the same intermediate in the transformation of **38** to **38** could give rise to **34** (Scheme 29).



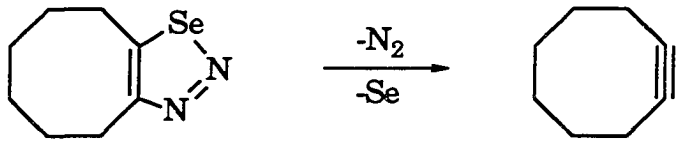
37

34

Scheme 29

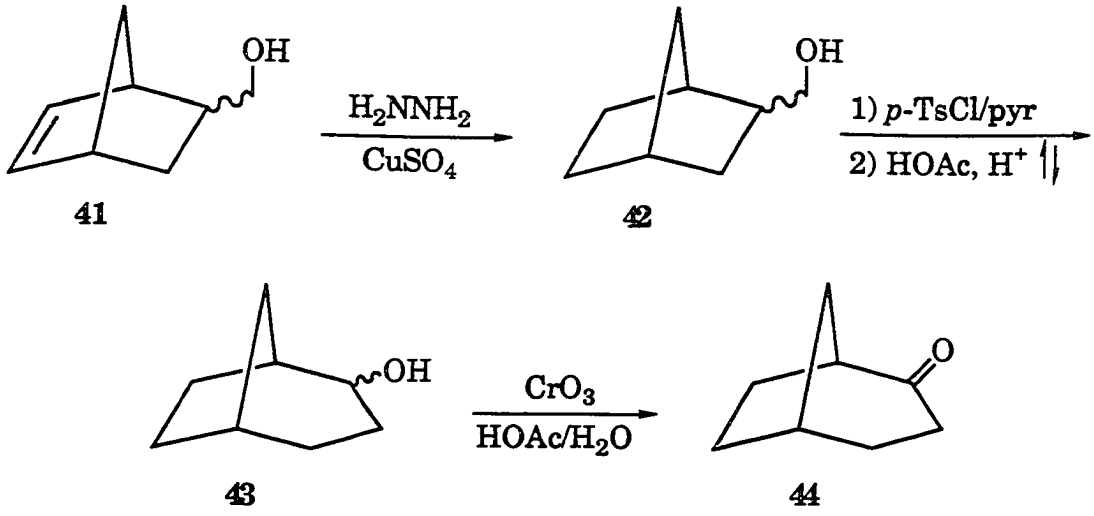
In order to eliminate the ring expanded alkyne as a possible intermediate in the reaction bicyclo[3.2.1]oct-2-yne was generated by an established method.

Selenadiazoles have been demonstrated to thermally eliminate molecular nitrogen and selenium to form cyclic alkynes[32] (Scheme 30).

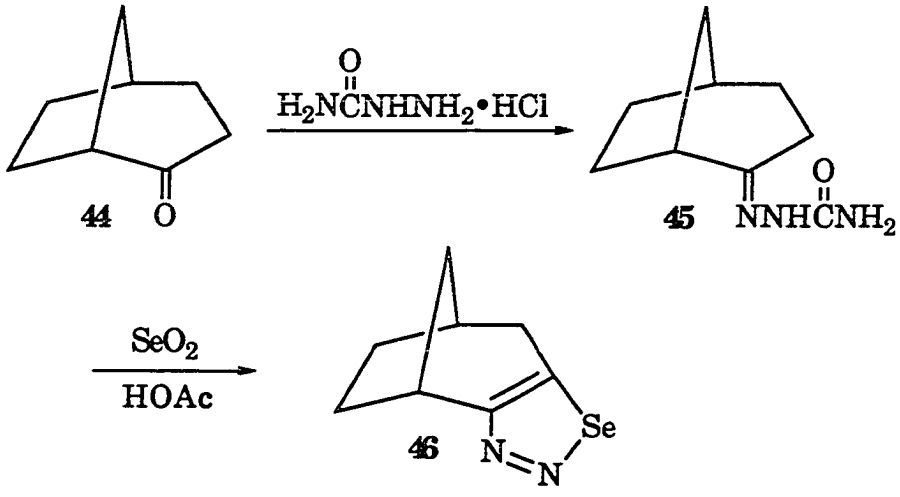


Scheme 30

Meier reported[32] the synthesis of selenadiazoles by ring closure of the semicarbazone by the action of selenous acid. Thus, ketone **44** was prepared in three steps from readily available 5-methanol bicyclo[2.2.1]hept-2-ene **41**. Reduction of **41** with hydrazine gave alcohol **42** in 97% yield. The alcohol was converted to the tosylate and then ring expanded by the method of Nedenskov and coworkers,[33a] in 86% yield. The resulting alcohol **43** was converted to the ketone **44** by chromic acid oxidation[33b] in 73% yield (Scheme 31).



Scheme 31

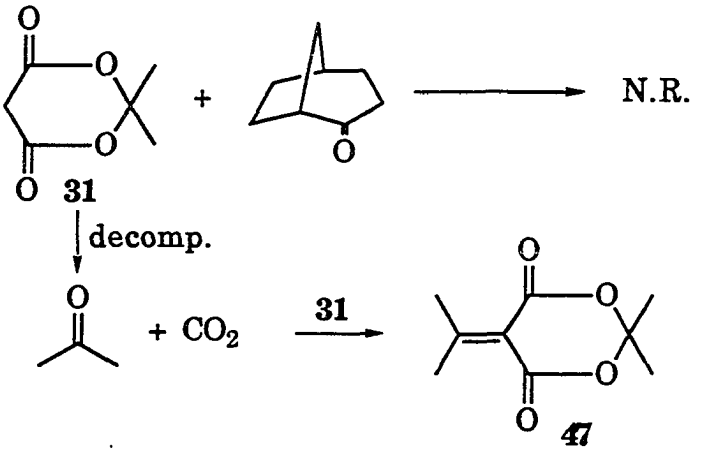


Scheme 32

The ketone **44** was converted to the semicarbazone **45** by the method described by Meier,[32] however ring closure by the prescribed[32] method was ineffective. Changing the solvent from the dixoane/water system to glacial acetic acid[34] afford a fair yield of the desired selenadiazole **46** (Scheme 32).

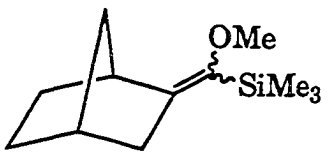
Selenadiazole **46** was subjected to FVP at 600 °C and 10^{-5} mmHg. The starting material was completely consumed. GC and GC/IR/MS indicated formation of at least fourteen products with low (≤160 amu) molecular weight. Three of these had mass of 106. Mass spectra and infrared spectra did not match the products formed in the vinylidene reaction, demonstrating the ring expanded alkyne is most likely not an intermediate formed from the vinylidene.

Several attempts were made to condense bicyclo[3.2.1]octan-2-one **44** with Meldrum's acid **31** but were unsuccessful. Under the reaction conditions which successfully produced the desired derivative of norcamphor, Meldrum's acid decomposed without forming a derivative with the ketone. The reaction gave 5-(ω,ω-dimethylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **47**.



Scheme 33

It was hoped that a precursor could be prepared that would decompose at a lower temperature than the Meldrum's acid derivatives (ca. 625 °C) in order to observe, or at least trap, primary reaction products. Alpha elimination of trimethylsilyl alkoxides and halides are known to product vinylidens. Therefore, a molecule such as would be a useful synthetic target.[35]



This class of compounds offers the additional advantage of undergoing fluoride-induced elimination,[36] therefore solution reactions and solid-supported reagent reaction might be accessible.

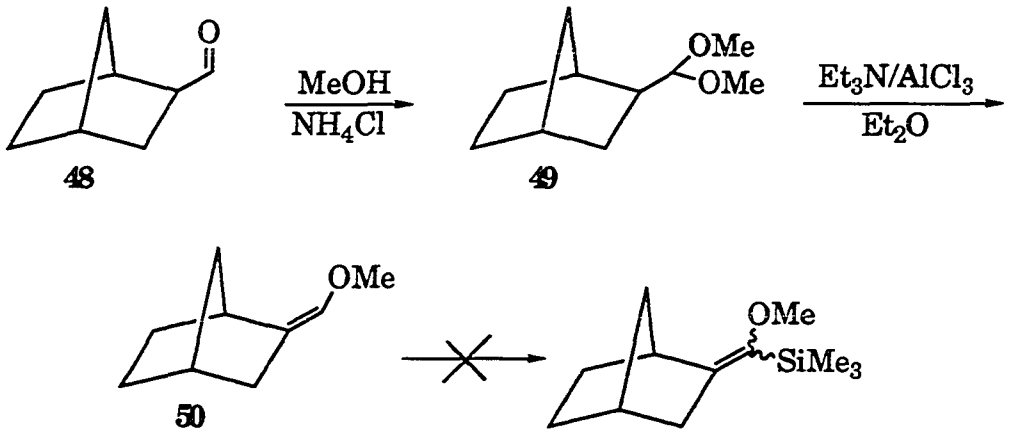
The first synthetic strategy was to convert 2-methanolnorbornane **41**, which was available from a previous synthesis, to the corresponding methylvinyl ether and then silylate it in the fashion applied to simpler systems[37] (Scheme 34).

To this end the alcohol **41** was oxidized to aldehyde **48** with pyridinium chlorochromate.[38] The aldehyde **48** was dissolved in dry methanol with a catalytic amount of anhydrous ammonium chloride.[35] Disappearance of the aldehyde, and formation of the acetal **49**, was monitored by analytical GC. When the conversion was complete extraction and sovlent removal gave a 96% yield of the pure acetal **49**.

Methanol was eliminated from acetal **49** by the methods of Barbat and Migionac[39a] using triethylamine and either magnesium bromide in benzene or aluminum chloride in ether. Yields of only 12% were realized in either case but the aluminum chloride/ether system gave a clean conversion and the methylvinyl **50** ether was easily isolated in pure form.

Attempts to silylate **50** can best be described as frustrating. The ether appeared to be resistant to lithiation. Deuterium oxide quenching of reaction mixtures of *tert*-buytl lithium in either ether or tetrahydrofuran, with or

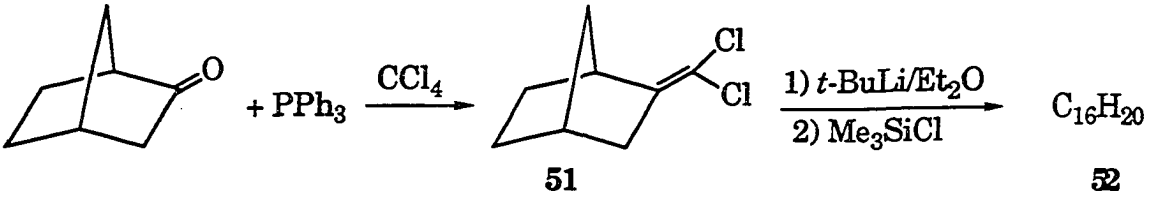
without triethylamine, showed no deuteration of the methyl vinyl ether. Only when the starting material with *tert*-butyl lithium in tetrahydrofuran was allowed to warm to room temperature before quenching with trimethylchlorosilane was the starting material consumed, however, none of the desired product was formed.



Scheme 34

As an alternative to the methylvinyl ether approach, ω,ω-dichloromethylenenorbornane **51** was prepared in good yield by the Wittig reaction of norcamphor and triphenylphosphine in carbon tetrachloride.

Again, attempts to silylate the methylene norbornane were unsuccessful. Treatment of **51** with *tert*-butyl lithium in ether at -115 °C and allowing the mixture to warm to after 2 hours at -115 °C afforded starting material and a very small amount of what appeared by GC/FTIR/MS to be the dechlorinated coupling product **51** (Scheme 35).



51 52

Scheme 35

The dichloride failed to react with magnesium in refluxing tetrahydrofuran or with trichlorosilane with catalytic chloroplatinic acid.

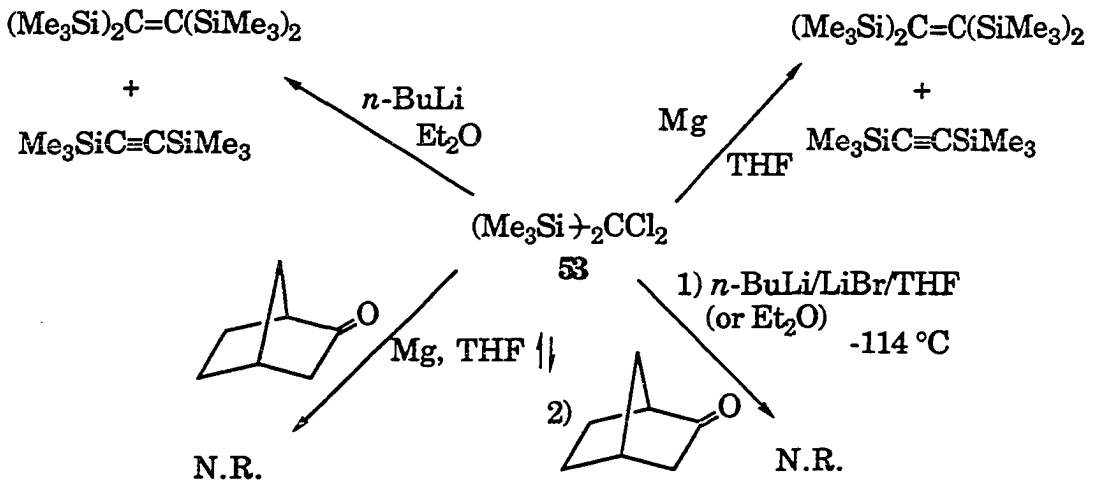
In an attempt to trap the precursor to the coupling product **52**, the lithiation was repeated with cyclohexene added as a vinylidene trap. In ethyl ether, or tetrahydrofuran no trapped vinylidene was observed. In toluene, only starting material was recovered. Apparently the coupling does not involve a free vinylidene. Very recently Nomura and coworkers have reported indium trialkyls to be useful reagents for cross-coupling of allenyl halides.[39b] If this methodology is extendable to indium silanes it would be a convenient route to the target molecule.

In hopes that a different synthetic approach would meet with better success several attempts at Peterson olefination of norcamphor were made. Bis(trimethylsilyl)dichlorosilane **53** was prepared by a Grignard coupling of trimethylchlorosilane and carbon tetrachloride.[40] Although substantial quantities of tris(trimethylsilyl)methane **54** were formed in the reaction, useful quantities of the dichloride were obtained and purified by preparative GC.

When the dichloride **53** was allowed to react with magnesium, coupling products, tetrakis-(trimethyl)ethene and bis(trimethylsilyl)acetylene, were formed before the reaction was quenched. In an effort to avoid coupling

norcamphor was added to the mixture. This apparently inhibited the formation of the Grignard as no reaction was then observed. Activation of the magnesium with either iodine or dibromomethane failed to effect the desired results.

Salt formation and coupling products demonstrated that the dichloride would react with magnesium in tetrahydrofuran, however, quenching with acetone, hexylbromide, or deuterium oxide afforded none of the expected products. Only coupling products were evident by GC/FTIR/MS analysis of the quenched aliquots (Scheme 36).

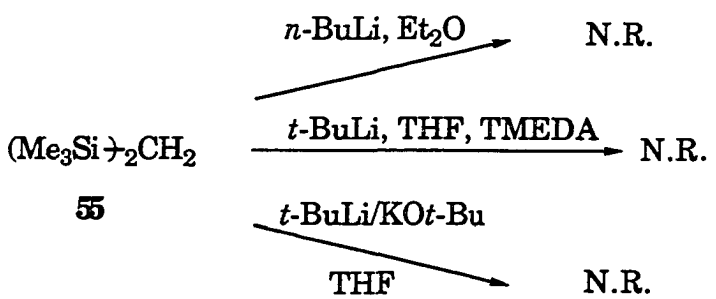


Scheme 36

Attempts to effect the olefination using *n*-butyl lithium in ether next with the same results. By analogy to chemistry of Villieras and coworkers,[41] attempts were made to lithiate the dichloride **53** in tetrahydrofuran or ether in the presence of lithium bromide. No reaction was apparent.

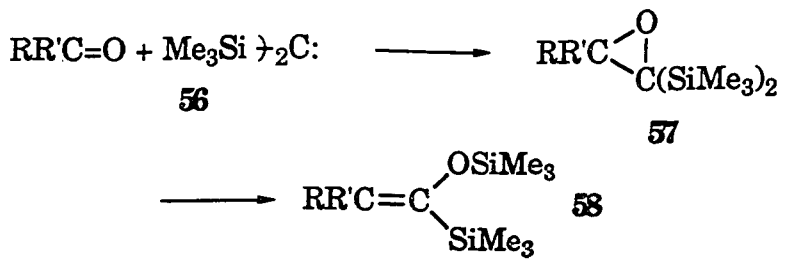
As an alternative to the dichloride, bis(trimethylsilyl)methane **55** was synthesized by magnesium coupling of trimethylchlorosilane with methylene chloride in tetrahydrofuran.[40]

n-Butyl lithium in ether, *tert*-butyl lithium in tetrahydrofuran with tetramethyl ethylene diamine,[42] and *tert*-butyl lithium/potassium *tert*-butoxide in tetrahydrofuran all failed to lithiate bis(trimethylsilyl)methane **55** (Scheme 37). The failure of *n*-butyl lithium in ether and of the *tert*-butyl lithium-potassium *tert*-butoxide to abstract the reduced reactivity of agrigated organo lithium compared to the monomeric form. The failure of the TMEDA complexed *t*-BuLi to react is quite bothersome. It should, and has been demonstrated[42] to, lithiate this very silane. It probably reflects a shortcoming of experimental technique rather than the reaction.



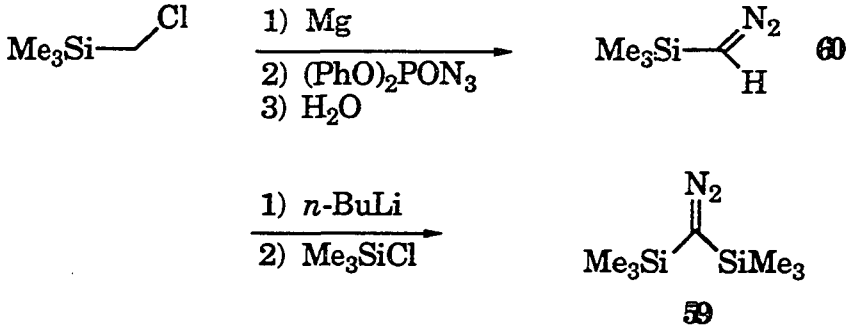
Scheme 37

Hoekman[43] reported the formation of an epoxide in the trapping of bis(trimethylsilyl)carbene by benzaldehyde in the photodecomposition of bis(trimethyl-silyl)diazomethane **59** (Scheme 38, R = H, R' = Ph). It was hoped that this strategy would allow trapping of ketones which could then be converted to α-silyl-α-siloxymethylene bicycle (also Scheme 38).



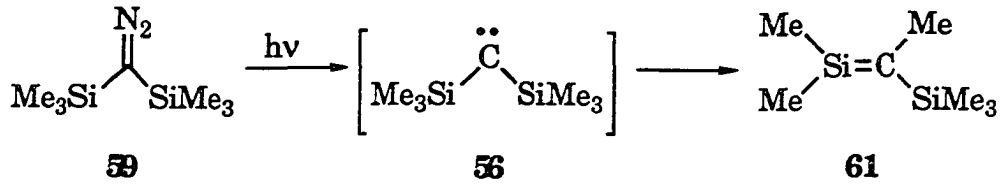
Scheme 38

Trimethylsilyldiazomethane **60** was readily available by the method of Mori et al.[44] Bis(trimethylsilyl)diazomethane **59** was accessed by a slightly modified version of Sekiguchi and Ando's method for bis(silyl)diazomethane synthesis[45] (Scheme 39).



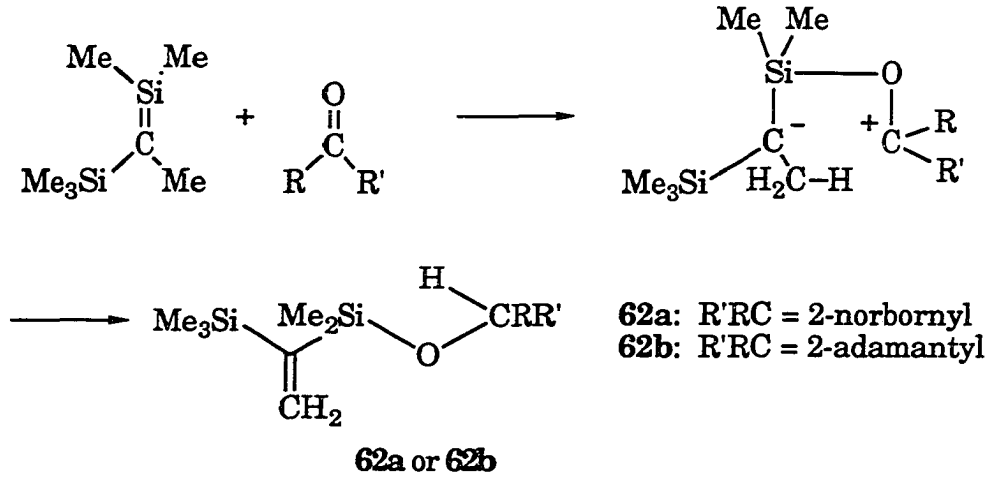
Scheme 39

The bis(trimethylsilyl)diazomethane **59** was photolyzed in hexane solutions, in separate runs, with norcamphor and adamanatanone. In both cases it appeared that the carbene **56** rearranged to the silene **61**, a known rearrangement, before it could be trapped (Scheme 40). The silene was then trapped (Scheme 41).



59 56 61

Scheme 40



62a: R'RC = 2-norbornyl
62b: R'RC = 2-adamantyl

62a or 62b

Scheme 41

The procedure previously described[43] for epoxide formation from benzaldehyde was repeated. (A 10% solution of the diazomethane **59** in deuterated benzene with an equivalent of benzaldehyde was irradiated 2 hours). NMR analysis of the sample showed no peaks that could be attributed to an epoxide were observed. After an additional 5 hours of irradiation produced no change in the spectrum.

EXPERIMENTAL

Instrumentation

High resolution ^{1}H (300 MHz) and ^{13}C (75.4 MHz) nuclear magnetic resonance (NMR) spectra were recorded on Nicolet NT-300 or Varian-300 spectrometers. All chemical shifts are reported in parts per million from tetramethylsilane and the solvent used is deuterated chloroform unless stated otherwise. Designation of coupling and integration is by the standard abbreviations.

Electron impact mass spectra were recorded using a Hewlett Packard 5970B mass selective detector operating at 70eV and are reported as m/z (% relative intensity).

Infrared spectra were recorded on an Biorad FTS-7 FTIR spectrophotometer or a Hewlett Packard 5965A infrared detector and are reported in wave numbers.

Quantitative gas chromatography (GC) analyses were performed on a Hewlett Packard 5890A gas chromatograph equipped with a flame ionization detector (FID) and a recording integrator and using a 30 meter, 0.25 mm i.d., capillary column with a 0.25 μm DB-5 coating. Helium was used as the carrier gas.

Preparative gas chromatographic separations were performed on a Varian 920 gas chromatograph using 8 to 9 foot 1/4 inch copper columns packed with 15% SE-30 on chromosorb W. The instrument was equipped with a thermal conductivity detector and a chart recorder. The carrier gas was helium.

General conditions for flash vacuum pyrolysis (FVP)

All samples were vacuum distilled from a bath maintained at a temperature allowing the slow introduction of the sample into a horizontal quartz tube packed with irregular sized quartz chips and heated with an electric tube furnace. The 1.6 cm x 30 cm heated zone of the quartz tube was maintained at constant temperature by a temperature controller. Pyrolysates were collected in a cold trap cooled by liquid nitrogen. Pressures were measured with an ionization gauge behind two liquid nitrogen traps and are, therefore, only reflective of the actual pressures in the pyrolysis zone.

General conditions for flow pyrolyses

The oven and furnace were the same as used for the FVP with the exception that the tube was positioned vertically rather than horizontally. The pyrolysis tube was swept with a 40 mL/min stream of nitrogen throughout the addition unless otherwise specified. The pyrolysates were collected in a trap cooled by dry ice.

General conditions for stirred-flow reactor (SFR) pyrolyses

The pulsed stirred-flow reactor used was a modification of the design of Baldwin et al.[46] A 3 cm^3 quartz reactor, swept by a stream of helium, was maintained at constant temperature by a Digi-Sense temperature controller. The reactor was ported for syringe-injected introduction of liquid samples into the hot-zone. The product stream was fed into the injection port of a Hewlett Packard 5890A gas chromatograph equipped with serially configured Hewlett Packard 5970B mass selective (MSD) and 5965A infrared detectors (IRD).

Similarly, an SFR was connected to a GC equipped with parallel configured FID and MSD.

General conditions for photolyses

All reactions were conducted in quartz vessels suspended in an Rayonet Model RPR-100 UV reactor equipped with sixteeen 2573 Å bulbs. the temperature within the reactor was maintained at ca. 40 °C by use of the cooling fan. Samples and solvents were degassed by either bubbling argon through the solution or the freeze/thaw technique.

General method for molecular mechanics calculations

All calculations were performed using the 1987 version of PC MODEL. This is an MM2 program[25] ported for IBM PC's and modified by Serena Software. In an attempt to ensure location of global minima multiple conformational isomers were examined, and while there is no rigorous way to demonstrate that the global minimum was found in each case, because of the limited number of minima available to systems as small as those calculated, it is believed that the energies reported correspond to the lowest energy conformation.

The concept of olefinic strain (OS) was applied to certain systems. In these cases the total strain energy of the saturated system in its lowest energy conformation was subtracted from that of the unsaturated system in its lowest energy conformation. While preferrred conformation may differ this is believed to be a realistic approach to energy comparison.

Calculation of energies for Table I

Two conformations of methylcyclopentane gave energies of 11.61 and 12.77 (kcal mol^{-1}). Only one minimum could be located for methylene cyclopentane, 10.80.

Twisted boat and chair conformation of cyclohexane gave 11.91 and 6.565, respectively. Cyclohexyne gave 30.80.

Axial and equatorial methylcyclohexane gave 12.77 and 11.61, respectively. Methylenecyclohexene fell to two minima, one at 11.25 and the other at 6.04.

Cycloheptane gave only one minima, 14.31. Cycloheptyne gave 20.39.

Methylcycloheptane gave minima of 15.00 and 17.06 while methylene cycloheptane fell to 13.29 and 12.87.

Cyclooctyne gave minima of 22.53, 19.41, and 20.38.

Cyclooctane gave several conformations of 18.45 and two of 19.14.

The two conformations of 5-methylbicyclo[2.1.1]hexane gave 45.58 and 45.67 while the methylene analog gave 49.16.

Norbornane gave a minima of 23.09 and norbornyne gave 94.87.

2-Methylnorbornane gave 24.23 and the methylene analog gave 23.56.

Bicyclo[3.2.1]octane fell to 19.27 and 27.74 while the corresponding alkyne gave 45.72.

2-Methyladamantane fell to 19.53 while methyleneadamantane gave 17.46.

Homoadamantane gave 28.01 and homoadamantyne gave 28.01.

Synthesis of (ω-bromomethylene) adamantane **23**

A solution of lithium diisopropyl amide was prepared by adding 4 mL 2.5 M *n*-butyl lithium (10 mmol-Aldrich, in hexanes) to 1.01 g diisopropyl amine (10 mmol) in 5 mL tetrahydrofuran at 0 °C.

The freshly prepared lithium diisopropyl amide solution was added *via* syringe to a solution of 4.4 g (bromomethyl)triphenylphosphonium bromide (10 mmol-Aldrich, 98%) in 40 mL tetrahydrofuran (distilled from calcium hydride) under argon and at -78 °C. The solution thus formed was stirred at -78 °C for 1 hour, and then treated with a solution of 1.5 g adamantanone (10 mmol-Aldrich, 99%) in 10 mL tetrahydrofuran. The resulting opaque, orange mixture was allowed to warm to room temperature over a 2 hour period. The reaction mixture was vacuum filtered through 10 cm of silica gel over a glass frit and the solids washed with 25 mL methylene chloride. After removing the solvents by rotary evaporation products were separated by flash column (10% ethyl acetate in hexane) followed by preparative gas chromatography. Along with a non-brominate adduct, 480 mg of pure bromomethylene adamantane was obtained (21% yield). (ω-Bromo-methylene) adamantane **23** gave the following spectra: ^{1}H NMR 5.76 (s, 1H), 3.05 (s, 1H), 2.53 (s, 1H), 1.69-1.91 (m, 12H); ^{13}C NMR 152.5, 92.9, 39.6, 37.9, 36.8, 34.4, 28.0; FTIR 2924(s), 2862(m), 1452(w), 1274(w), 1099(w), 782(w); MS 228(100) 226(M^+, 97), 147(57), 119(32), 105(53), 91(87), 79(34), 77(23). Methylene adamantane **23a** gave the following spectra: ^{1}H NMR 4.46 (s, 2H), 2.44 (s, 2H), 1.7-1.9 (m, 12H); ^{13}C NMR 154.5, 100.5, 39.6, 39.0, 37.3, 28.3; FTIR 3073(w), 2920(s), 2861(m), 1451(w), 888(w); MS 149(13), 148(M^+, 100), 119(19), 105(33), 93(29), 92(58), 91(66), 79(44), 77(26).

Trapping of vinylidene adamantane **24** with cyclohexene

A solution of 143 mg (ω-bromomethylene adamantane **23** (0.63 mmol), 140 mg potassium *tert*-butoxide (1.25 mmol-Aldrich, 98%), and 450 mg cyclohexene (5.5 mmol-Aldrich, 99%) in 5 mL toluene (Fisher, HPLC grade, dried over calcium chloride) was degassed by freezing and thawing, and sealed. The sealed tube was heated at 100 °C for 5 h and then cooled and opened. The solvent was removed by rotary evaporation at ca. 80 °C. The products were isolated by preparative GC. Only 26 mg cyclohexene trapped vinylidene **24b** and 34 mg *tert*-butyl alcohol trapped vinylidene **24a** were isolated. Actual yields were undoubtedly higher. The cyclohexene trapped vinylidene **24b** gave the following: ^{1}H NMR 2.62 (s, 1H), 1.6-2.0 (m, 16H), 1.50 (m, 2H), 1.1-1.3 (m, 4H); ^{13}C NMR 135.8, 116.7, 39.4, 39.3, 38.9, 37.5, 36.7, 28.9, 28.5, 23.1, 21.6, 12.0; FTIR 2985(w), 2919(s), 2861(m), 1452(w), 1097(w); MS 229 (18), 228 (M^+, 100), 213 (21), 200 (16), 185 (49), 171 (28), 129 (30), 117 (34), 105 (21), 91 (50), 79 (32). The *tert*-butyl alcohol trapped vinylidene **24a** gave the following spectra: ^{1}H NMR 5.91 (s, 1H), 2.98 (s, 1H), 2.23 (s, 1H), 1.65-1.95 (m, 12H), 1.20 (s, 9H); ^{13}C NMR 131.1, 127.0, 75.0 39.9, 38.4, 37.4, 34.5, 29.1, 28.9, 27.8; FTIR 2982(m), 2917(s), 2859(m), 1677(w), 1393(w), 1370(w), 1192(m), 1133(s), 1098(w); MS 220 (M^+, 7), 165 (11), 164 (100), 135 (7), 107 (14), 91 (10), 79 (13).

Attempted trapping of homoadamantyne **22** with diphenylisobenzafuran (DPIBF)

A mixture of 113 mg (ω-bromomethylene) adamantane **23**(0.5 mmol), 452 mg potassium *tert*-butoxide (4.0 mmol-Aldrich), and 625 mg DPIBF (2.3 mmol-Aldrich) in 5 mL toluene (Fisher, HPLC grade, dried over calcium chloride)

was degassed by freezing and thawing and sealed. The sealed tube was heated at 100 °C for 5 h. The salts were removed by filtration and the solution stripped at high vacuum and then replaced with deuterated chloroform. ^{13}C NMR showed only peaks corresponding to the DPIBF in the aromatic region and *tert*-butyl alcohol trapped vinylidene **24a**. No other products were evident by GC/FTIR/MS or by TLC analysis.

Synthesis of the Meldrum's acid derivative of noncamphor **32**

Method A: A mixture of 3.0 g (27 mmol) norcamphor **30** and 3.9 g (27 mmol-Aldrich 98%) 2,3-dimethyl-1,3-dioxane-4,6-dione **31** in 10 mL pyridine (Fisher, ACS, dried 24 h over activated 4Å molecular sieves) and 1.5 g 4Å molecular sieves (Fisher) was stirred in a 25 mL round-bottom flask for 24 hours. The pyridine solution was decanted from the molecular sieves and the lower boiling components stripped by rotary evaporation. The residue was taken up in 10 mL ethyl ether, filtered, and washed with 10 mL portions of saturated sodium bicarbonate and brine. After drying over sodium sulfate, the ether was stripped and the residue was distilled at room temperature and 10^{-4} mmHg to remove the unreacted norcamphor. The residue consisted of 1.11 g of 85% product **32** (GC purity-ca. 14% yield).

Method B: A mixture of 3.0 g (27 mmol) norcamphor **30** and 3.9 g (27 mmol-Aldrich 98%) 2,2-dimethyl-1,3-dioxane-4,6-dione **31** in 10 mL pyridine (Fisher, ACS, dried over 4Å molecular sieves) was stirred in a 25 mL round-bottom flask for 24 hours. The reaction mixture was stripped of pyridine and the residue taken up in ethyl ether. The solution was filtered through a 10 cm

plug of silica gel and the solvent removed leaving 3.34 g of 85% product **32** (ca. 41% yield). The primary impurity was unreacted dioxane **31**.

Method C: A solution of 9.6 g titanium tetrachloride (Fisher, ACS) and 15 mL carbon tetrachloride was added *via* syringe to 15 mL tetrahydrofuran (Fisher, ACS, distilled from calcium hydride) over a 15 minute period, at 0 °C, under argon, in an oven-dried 100 mL flask. A yellow precipitate formed. To this mixture, still at 0 °C, was added a solution consisting of 2.76 g norcamphor **30** (25 mmol) and 3.6 g 2,2-dimethyl-1,3-dioxane-4,6-dione **31** (25 mmol) in 15 mL tetrahydrofuran *via* syringe over a 10 minute period. Immediately there after a solution of 12 mL pyridine in 15 mL tetrahydrofuran was added over a 10 minute period. The mixture turned brown as the pyridine solution was added. It was allowed to warm to room temperature over a 2 hour period and was left stirring to react overnight. The reaction mixture was cooled to 0 °C and was quenched by addition of 10 mL water and was diluted with 60 mL ethyl ether. After separation from the aqueous portion, the organic material was washed with 50 mL each dilute hydrochloric acid, saturated sodium bicarbonate, and brine. The ether solution was dried over sodium sulfate and the solvent removed by rotary evaporation. The oily brown residue was purified by elution through a flash column with 4:1 hexane/ethyl acetate leaving 2.50 g of the desired adduct (ca. 42% yield). An analytical sample was recrystallized from methylene chloride/pentane giving white needles, MP = 86-87 °C. The adduct **32** gave the following spectra: ^{1}H NMR 4.24 (d, 1H, J= 4.8), 2.81 (d, 1H, J=3.6), 1.92 (m, 2H), 1.66 (s, 6H), 1.44 (m, 3H), 1.25 (m, 3H); ^{13}C NMR 194.0, 161.4, 161.1, 108.5, 103.6, 47.2, 45.0, 39.6, 35.4, 27.5, 27.3 (2c), 26.5; FTIR 2974(m), 2888(m), 1752(s), 1615(m), 1393(w), 1270(s), 1212(s), 1005(m),

922(m); MS 236 (M^+, 1), 221(6), 179(54), 178(100), 150(95), 134(76), 106(35), 105(30), 91(25), 66(42); UV π_{max} = 248 nm.

Pyrolysis of the Meldrum's acid derivative of norcamphor **32**

A 1.313 g sample of **32** was allowed to distill through the hot zone of the flash vacuum system at 625 °C and 10^{-5} mmHg over a 6 hour period. The trapped product consisted of 0.936 g brown liquid (71% mass recovery). GC/FTIR/MS analysis of the product mixture indicated acetone to be the major constituent along with smaller amounts of carbon monoxide and carbon dioxide. The three remaining principle components (ca. 15% of the mixture) were separated by preparative GC. Found in the ratio of 1.5:1:0.5, products **33**, **34**, and **35** gave the following spectral data: 3-vinyl-4-methylene cyclopentene **33** gave the following spectra: ^{1}H NMR (CD_2Cl_2) 6.85 (m, 1H), 5.70 (m, 1H), 4.9-5.1 (m, 5H), 3.84 (d, 1H, J=8.1), 3.12 (s, 2H), 1.59 (s, 1H); ^{13}C NMR (CD_2Cl_2) 152.0(s), 140.4(d), 133.1(d), 130.1(d), 113.9(t), 108.2(t), 55.1(d), 38.8(t); FTIR 3077(s), 299(w), 2910(m), 1646(m), 1427(w), 987(2), 895(s); MS 106 (M^+, 18), 105(20), 103(9), 91(100), 79(35), 78(51), 77(38), 65(22). 2-ethynyl-3-methyl cyclopentene **34** gave the following spectra: ^{1}H NMR 6.03 (q, 1H, J=2.1), 2.94(s, 1H), 2.73(dq, 1H, J=0.9, J=5.1), 2.33(m, 2H), 2.11(m, 1H), 1.40(m, 1H), 1.01(d, 3H, J=6.9); ^{13}C NMR 138.8(d), 129.3(s), 80.6(d), 78.9(s), 42.6(d), 32.1(t), 31.9(t), 19.5(q); FTIR 3092(m), 3018(m), 2933(s), 2862(w), 2227(w), 1835(w), 1611(m), 1441(w), 1331(m), 919(s); MS 105(16.5), 91(68), 78(55), 67(40), 65(100), 63(21). 2-vinyl-3-methylene cyclopentene **35** gave the following spectra: ^{1}H NMR (C_6D_6) 6.39 (ddd, 1H, J=1.5, J=15.9), 6.20 (s, 1H), 5.85 (s, 1H), 5.54, (dd, 1H, J=1.5, J=17.7), 5.08(dt, 1H, J=1.5, J=11.1), 4.88(d, 1H, J=0.9), 2.45(m, 2H), 2.12(s, 3H); ^{13}C NMR

(C_6D_6) 150.9(s), 136.6(d), 130.3(d), 126.4(d), 115.9(t), 101.5(t), 31.4(t), 30.2(d); FTIR 3092(w), 3058(w), 3011(m), 2936(s), 2860(m), 1633(m), 1431(w), 991(w), 918(m), 869(m); MS 106 (M^+, 51), 105(35), 91(100), 79(34), 78(54), 65(21).

Reduction of 5-methanol norbonyl-2-ene **41**

A solution of 41.7 g 5-methanol norboronyl-2-ene **41** (336 mmol) and 2.5 g copper(II) sulfate (15 mmol-Fisher, ACS) in 275 mL absolute ethanol was fitted with an air bubbler, Friedrichs condensor, and magnetic stirrer. At room temperature 100 g anhydrous hydrazine (3.13 mol-Aldrich, 98%) was added dropwise over a 1.5 hour period at a rate such that the solution did not become hot. The solution became brown as the hydrazine was added.

After 28 hours the solution was diluted with 200 mL ethyl ether and was decanted from the solids in the reaction mixture. The organic material was washed twice with 100 mL water and once with 100 mL brine. The washings were back extracted with 100 mL ethyl ether and the combined organic layers were dried over sodium sulfate. The ether was removed by rotary evaporation leaving 42.7 g clear viscous liquid which was 96% (GC) pure (97% yield). 2-Methanol norbornane **43** gave the following spectra: ^{1}H NMR 3.41 (m, 2H), 2.18 (m, 2H), 2.0 (bs, 1H), 1.0-1.7 (bm, 8H), 0.56 (ddd, J=2.1, J=5.4, J=12.3); ^{13}C NMR (2 sets) 65.0, 42.4, 39.7, 37.7, 36.6, 33.6, 29.9, 2.5, and 66.8, 44.78, 38.0, 36.0, 35.1, 33.9, 29.8, 28.9; FTIR 3665 2), 2959(s), 2882(m), 1465(w), 1051(m), 1014(m); MS 108(4), 95(100) 93(35), 79(41), 66(88). The ^{1}H NMR is complicated by the superimposition of the *exo* and *endo* (ca. 1:3) isomers. This also causes a pair of ^{13}C spectra which are distinguishable by gated acquisition.

Synthesis of bicyclo[3.2.1]octan-2-ol 43

A solution of 24.5 g 2-methanol norbornane **42** (194 mmol) in 20 mL pyridine (Fisher ACS, dried over 4Å molecular sieves) was added at once to a solution of 42.5 g *p*-toluene sulfonyl chloride (223 mmol-Aldrich, 98%) in 50 mL dry pyridine, all at room temperature and under argon in a 250 mL round-bottom flask. A precipitate formed immediately and an ice bath was required to moderate the reaction. The reaction mixture solidified. It was allowed to warm to room temperature and was left standing for 24 hours. The now liquid mixture was poured over ice and concentrated hydrochloric acid (Fisher) was added until the pH of the solution was 3.5. The tosylate was extracted with 125 mL ethyl ether and the ether washed with water until the washings came back with pH 6. The extract was dried over anhydrous sodium sulfate and the solvent removed by rotary evaporation.

The crude tosylate was combined with 60 mL acetic acid (Fisher, glacial), 0.5 g *p*-toluene sulfonic acid (3 mmol), and 225 mL water. The solution was refluxed 24 hours. After cooling to room temperature the product was exhaustively extracted with pentane and the pentane extract dried over anhydrous sodium sulfate. Solvent removal gave 20.8 g white crystals, M.P.=142-160 °C (86% yield) as a mixture of *exo* and *endo* isomers. Spectral data were consistent with alcohol **43**: FTIR 3650(w), 2943(s), 2877(m), 1462(w), 1062(m); MS 106 (M^+, 7), 108 (26), 95 (39), 93 (32), 80 (78), 79 (47), 67 (100), 57 (32).

Oxidation of bicyclo[3.2.1]octan-2-ol 43 to bicyclo[3.2.1]octan-2-one 44

At room temperature, 25.5 g bicyclo[3.2.1]-ocan-2-ol **43** (0.20 mol) dissolved in 26 mL acetic acid (Fisher, glacial) was slowly added to a solution of

17.8 g chromium trioxide (0.18 mol-Fisher, ACS) in 26 mL acetic acid and 15 mL water. The mixture was allowed to stir at room temperature overnight and then exhaustively extracted with pentane. After dry the extract over anhydrous sodium sulfate and solvent removal, 18.3 g product 44 (98% GC purity) was recovered as white crystals, M.P.=169-172 °C (73% yield). Spectral data were as follows: ^{1}H NMR broad and overlapping peaks from 1.1-2.7 ppm; ^{13}C NMR 214.1, 50.9, 38.0, 34.4, 33.7, 31.8, 27.7, 27.6; FTIR 2951(s), 2881(m), 1736(s), 1459(vw); MS 125(2), 124(M^+, 25), 106(1), 95(9), 80(100), 67(79).

Synthesis of bicyclo[3.2.1]octan-2-one semicarbazone 45

A solution of 1.5 g semicarbazide hydrochloride (13.5 mmol-Aldrich) and 2.0 g sodium acetate (24.4 mmol-Fisher, anhydrous, ACS) in 15 mL dry ethanol (dried over 4 Å molecular sieves, sequentially) was refluxed for 15 minutes. After to room temperature the salts were filtered from the solution. The filtrate was added to 1.24 bicyclo[3.2.1]octan-2-one 44 (10 mmol) and the resulting solution was refluxed for 2 hours. The solution was cooled to room temperature and 15 mL water was added. After standing overnight 1.14 g white crystals were isolated by filtration and air dried (M.P. = 168-170 °C; 63% yield). The spectral data are: ^{1}H NMR (CD_2Cl_2) 5.94 (bs, 1H), 5.39 (bs, 2H), 2.78 (s, 1H), 2.54 (dd, 1H, J=6.3, J=16.2), 2.34 (bs, 2H), 2.09 (d, 1H, J=6.9), 1.4-2.0 (m, 7H); ^{13}C NMR 158.2, 156.9, 44.2, 37.8, 33.6, 30.7, 29.1, 27.1, 19.7. The apparent dimer gave the spectra: FTIR 2954(s), 2875(m), 1589(w), 1450(w), 1318(w); MS 372(69), 370(68), 368(41), 292(42), 263(80), 195(67), 183(37), 155(23), 141(27), 115(32), 105(30), 91(55), 77(100).

Synthesis **46** of the selenadiazole derivative of bicyclo[3.2.1]oct-2-one

A mixture of 0.55 g selenium dioxide (5 mmol-Aldrich, 99%) and 0.9 g bicyclo[3.2.1]octan-2-one semicarbazone **45** (5 mmol) in 9 mL acetic acid (Fisher, glacial) was stirred at room temperature in the dark for 1.5 hours. Gas evolution was monitored by means of a bubbler. When gas evoluation had ceased the mixture, now deep red, was diluted with 20 mL chloroform and was washed with three 20 mL portions of water and then neutralized by washing with saturated sodium bicarbonate. After drying over sodium sulfate the chloroform was removed and 0.20 g product (20% yield) separated from the dark brown residue by column chromatography (1:4/ethyl acetate: hexane on silica). The product slowly decomposed at room temperature to the selenarene dimer (base on MS only). The product gave the following spectral data: ^{1}H NMR 3.88 (s, 1H), 3.06 (dd, 1H, J=3.9, J=17.7), 2.79 (dd, 1H, J=1.8, J=17.7), 2.63 (s, 1H), 1.3-2.1 (m, 6H); ^{13}C NMR 165.0, 153.5, 36.2, 35.4, 35.3, 35.2, 33.7, 29.1; FTIR 2962(s), 2881(w), 1747(m), 1368(w), 1322(m), 1014(w); MS 186 (M^{+}-28, 42), 159(20), 158(20), 157(100), 155(47), 154(17), 153(18), 118(29), 105(57), 91(30), 78(68).

Pyrolysis of **46** the selenadiazole derivative of bicyclo[3.2.1]octan-2-one **46**

An aliquot of 230 mg of the selenadiazole **46** was subjected to FVP at 625 °C and 10^{-4} mmHg over a 20 minute period. The pyrolysate, 76 mg (33% mass recovery) very rank smelling, dark-reddish liquid, was analyzed by GC/FTIR/MS. At least fourteen products were evident by the overlapping peaks. Three isomers of the vinylidene (M^{+}=106) gave the following spectra: **A** gave MS 106 (M^{+}, 37), 105(22), 91(100), 78(56), 65(23); FTIR 3078(s), 2992(m), 2926(s), 2863(w), 1936(s), 989(m), 914(s), 874(s), 770(m); **B** gave MS 106 (M^{+}, 37),

105(27), 103(14), 91(100), 79(26), 78(80), 77(32), 65(10); FTIR 3059(w), 2948(s), 2854(m), 1636(w), 1447(w), 1322(w), 913(w); **C** gave MS 106 (M^+, 49), 105(23), 104(20), 91(100), 79(34), 78(64), 77(36), 65(19); FTIR 3043(s), 2937(s), 2889(s), 1607(w), 1373(w), 1373(w), 1187(w), 958(s), 897(s), 817(s). Other prominent peaks in the GC/FTIR/MS trace gave FTIR 1657(w), 1294(s); MS 172(100), 92(28), 80(59) // FTIR 2967(19), 2890(w), 1660(w), 883(w); MS 108(24), 106(14), 93(39), 79(100), 77(54) // FTIR 3061(s), 2926(s), 1452(w), 922(w), 818(w), MS 145(55), 117(6), 106(48), 91(100), 78(87), 65(29) // FTIR 3077(s), 3028(s), 2932(w), 1825(w), 1631(w), 1440(w), 912(s), 773(s); MS 104(100), 103(46), 78(66), 77(27), 63(11) // FTIR 3075(m), 2927(s), 1630(m), 1476(m), 811(s); MS 160(7), 145(6), 104(70), 103(58), 78(100), 63(13).

Attempted condensation of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's Acid) and bicyclo[3.2.1]octan-2-one 44

Method A: A mixture of 1.0 g bicyclo[3.2.1]octan-2-one 44 (8 mmol) and 1.3 g 2,2-dimethyl-1,3-dioxane-4,6-dione (9 mmol-Aldrich 98%) in 3.5 mL pyridine (Fisher, ACS, dried over 4Å molecular sieves) was stirred at room temperature for 2 days. GC/IR/MS analysis revealed formation of the condensation of the dione with acetone rather than the bicycle.

Method B: A solution of 3.2 g titanium tetrachloride (Fisher, ACS) and 5 mL carbon tetrachloride was added *via* syringe to 5 mL tetrahydrofuran (distilled from calcium hydride) over a 15 minute period at 0 °C under argon. To this mixture was added a solution consisting of 1.0 g bicyclo[3.2.1]-octan-2-one (8 mmol) and 1.2 g 2,2-dimethyl-1,3-dioxane-4,6-dione in 5 mL tetrahydrofuran over a 10 minute period. A solution of 4 mL pyridine and 5

mL tetrahydrofuran was added immediately thereafter. The solution was allowed to warm to room temperature and react overnight. Workup was before afforded only the starting ketone and 220 mg condensation product of Meldrum's acid and acetone, 5-(ω,ω-dimethyl methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **47**. A recrystalized (from hexane) sample of the condensation product **47** gave the following spectra: ^{1}H NMR 2.47 (s, 1H), 1.68 (s, 1H); ^{13}C NMR 177.1(s), 160(s), 115.6(s), 103.2(s), 26.9(q. J=128), 26.5(q, J=127); FTIR 3591(w), 3003(w), 2365(w), 2134(s), 1758(s), 1277(s), 1219(m); MS 169 (M^{+}-15, 4), 127(44), 109(16), 98(54), 82(100), 67(69), 58(85). Crystallographic data for the adduct **47** are: $O_4C_9H_{12}$, $P2_1/C$, a=8.677 (2) Å, b=10.9051 (7) Å, c=9.872 (1) Å, β=94.97 (2), V=930.6 (9) $Å^3$, Z=4, d calcd.=1.31 g/cm^3, $\mu(MoK_\alpha)$=1.0 cm^{-1}, 0.45 x 0.20 x 0.20 mm, θ-2θ scan, 3505 reflections collected, three strong reflection measured hourly indicating 1.3% intensity loss so decay correction applied, observed redundant data average gave 1.6% agreement factor (on F_{OBS}), 1735 unique data, 1276 with $F_{OBS}^2 > 3.06 > F_{OBS}^2$, direct methods, R = 0.034, R_w = 0.053.

Oxidation of 2-methanol norbornane **42** to 2-methanal norbornane **48**

A slurry of 26 g pyridinium chlorochromate (121 mmol-Aldrich, 98%) and 52 g Florisil (dried by heating at 100 °C and 2 mmHg for 24 hours) in 800 mL methylene chloride was stirred at room temperature for 2 hours. The alcohol, 10.4 g (82.5 mmol-96%) was added *via* syringe to the well stirred slurry at room temperature. The mixture changed from orange to brown during the addition. After 4 hours GC analysis showed none of the starting material. The mixture was filtered through anhydrous magnesium sulfate and the

solvent was stripped by rotary evaporation and replaced with 200 mL pentane. The precipitate was filtered and the pentane solution was dried over anhydrous sodium sulfate. Removal of the solvent by rotary evaporation gave 7.3 g of 67% pure (GC) aldehyde **48** as a clear yellow liquid (48% yield). The product was further purified by vacuum distillation (45-48 °C, 2.5 mmHg). The sample gave the following spectra: ^{1}H NMR 9.68 (d, 1H, J=0.9), 2.61 (m, 1H), 2.22 (m, 1H), 1.32-1.64 (m, 9H); ^{13}C NMR 205.1, 53.7, 40.0, 38.7, 37.1, 29.3, 29.2, 24.5; FTIR 2965(s), 2886(m), 2806(w), 2706(w), 1735(s); MS 124(M^{+}, 1), 106(15), 95(35), 91(19), 80(81), 67(100).

Synthesis of 2-methanal norbornane dimethylacetal **49**

At room temperature 7.02 g 2-methanalnorbornane **48** (57 mmol) was dissolved in 70 mL methanol (Fisher, ACS) and 1.1 g anhydrous ammonium chloride was added. The solution was stirred in a 100 mL round-bottom flask under argon for three days. GC monitoring indicated complete consumption of the starting aldehyde **48**. The reaction mixture was partioned between 30 mL each pentane and brine. The aqueous portion was extracted with an additional 30 mL pentane. The aqueous layers were combined and dried over anhydrous sodium sulfate. Solvent removal left 6.32 g of 96.7% pure (GC) acetal **49** (66% yield). The acetal (*exo/endo* mixture in a ratio of ca. 2.3:1 (or 1:2.3) ratio gave the following spectra: ^{1}H NMR 4.09 and 3.90 (pair d, 1H, J=9), 3.20 and 3.15 (pair s, 3H), 2.09 (broad m, 2H), 0.95-1.65 (broad d overlapping m's, 9H); ^{13}C NMR 106.8, 52.4, 44.0, 38.0, 36.3, 35.8, 33.2, 29.7, 28.6 and 106.2, 52.1, 41.4, 39.6, 38.2, 36.6, 32.8, 29.6, 23.4; FTIR 2960(s), 2884(w), 2837(w), 1122(m), 1075(m); MS 139(5), 109(4), 107(5), 79(10), 75(100), 67(6), 55(3).

Synthesis of 2-(ω-methoxymethylene)norbornane **50**

Method A: A mixture of 738 mg anhydrous magnesium bromide (4 mmol-Aldrich, 98%) and 404 mg triethylamine (4 mmol-Kodak, dried over molecular sieves) in 2.4 mL benzene (Fisher, ACS, drived over 4 Å molecular sieves) was stirred at room temperature for 30 minutes. A solution of 340 mg 2-dimethoxymethylnorbornane **49** and an equal volume of benzene was slowly added to the well stirred solution at room temperature. The resulting light tan suspension was refluxed 24 hours and then cooled to room temperature. GC/IR/MS analysis suggested the formation of the two desired isomers. The benzene was replaced with pentane and the salt removed by filtration through a magnesium sulfate plug. The pentane was then removed by rotary evaporation. Preparative GC yielded 34 mg of the desired isomers (12% yield). The product **50** (E/Z mixture in ca. 1:4 (or 4:1) ratio gave the following spectra: ^{1}H NMR 5.84 and 5.62 (t, ^{1}H, J=2.7), 3.27 and 3.22 (s, 3H), 2.54 (s, 1H), 1.88 (m, 1H), 1.1-1.6 (overlapping m's, 8H); ^{13}C 136.5, 124.1, 59.2, 40.8, 39.6, 36.4, 33.9, 30.7, 28.6; FTIR 2965(s), 2880(m), 2840(m), 1696(m), 1459(w), 1355(w), 1220(m), 1176(m), 1132(s); MS 139(2), 138(M^+, 19), 123(9), 109(100), 91(12), 79(14), 77(15).

Method B: A solution of 809 mg triethylamine (8 mmol-Kodak, dried over 4Å molecular sieves) in an equal volume of anhydrous ethyl ether (Fisher) was slowly added to a solution of 532 mg anhydrous aluminum chloride (4 mmol-Fisher, ACS). The resulting solution was stirred at room temperature under argon for 2 hours.

A solution of 340 mg of the acetal **49** (2 mmol) in an equal volume ethyl ether was slowly added to the amine-aluminum chloride solution. An oily

brown lower layer appeared immediately while the bulk of the solution was turbid white. After 6 hours GC analysis showed that the starting material was consumed and product formed. The solution was decanted from the oil and diluted with 20 mL pentane and washed with three 10 mL portions of water. After drying over anhydrous sodium sulfate the pentane was removed leaving 92 mg crude product **50** (87% pure by GC). Only 30 mg pure 2-(ω-methoxymethylene)norbornane **50** was isolated by preparative GC (12% yield). 2-(ω-Methoxy)methylenenorbornane gave the following spectra: ^{1}H NMR 5.84 (t, ^{1}H, J=2.7), 3.27(s, 3H), 2.54(s, 1H), 1.88(m, 1H), 1.1-1.6(m, 8H); ^{13}C NMR 136.5, 124.1, 59.2, 40.8, 39.6, 36.4, 33.9, 30.7, 28.6; FTIR 2965(s), 2880(w), 2840(w), 1697(w), 1220(w), 1175(w), 1132(m); MS 139(2), 138(20), 110(11), 109(100), 91(12), 79(14), 77(15), 67(17).

Attempted silylation of 2-(methoxymethylene)norbornane **50**

Method A: An oven-dried, argon flushed 10 mL round-bottom flask equipped with a magnetic stirrer and argon balloon was charged with 1 mL ethyl ether (Fisher, anhydrous), 10 μL, triethylamine, and 30 mg 2-(ω-methoxymethylene)norbornane **50** (0.22 mmol). After cooling to -78 °C the solution was treated with 0.51 mL 1.7 M *tert*-butyl lithium (0.87 mmol-Aldrich, in hexanes). The mixture was allowed to warm to 0 °C over a 2 hour period and then maintained at 0 °C for an additional hour during which time the clear yellow solution became clear white. The solution was cooled to -78 °C and 140 μL trimethylchlorosilane (1.1 mmol-Aldrich 98%) was added. The mixture was allowed to warm to room temperature and stir for 16 hours. GC and GC/FTIR/MS analysis of the mixture showed none of the desired product and

it appeared that most of the starting vinyl ether **50** was unreacted. *tert*-Butyl-trimethylsilane was evident in the reaction mixture.

Method B: The reaction was set up as above but this time was allowed to warm to room temperature after the addition of the *tert*-butyl lithium and then stirred overnight. Quenching with deuterium oxide and with trimethylchlorosilane suggested none of the vinyl ether **50** was lithiated.

Method C: The reaction was step up as above but this time was refluxed for 4 hours. Quenching with either deuterium oxide or trimethylchlorosilane again suggested that the vinyl ether **50** was not lithiated. *tert*-Butyl-trimethylsilane was present in the reaction mixture after the quench with trimethylchlorosilane.

Method D: The reaction was set up as in method A except the triethylamine was omitted. The result was the same.

Method E: The reaction was set up as in method D except tetrahydrofuran was substituted for ethyl ether. This time no starting material remained but none of the desired product was evident in the product mixture based on GC/FTIR/MS analysis of the mixture.

Synthesis of 2-(ω,ω-dichloromethylene)norbornane **51**

An oven-dried, argon flushed 25 mL round-bottom flask equipped with a condenser, drying tube, and magnetic stirrer was charged with 1.1 g norcamphor (10 mmol), 7.87 g triphenylphosphine (30 mmol-Kodak 98%), and 15 mL carbon tetrachloride (Fisher, ACS). The solution was refluxed for 1 hour at which time none of the starting ketone remained. The phosphine oxide was removed by flash column and 1.49 g product (98% pure-85% yield)

remained after rotary evaporation of the solvents. The product, 2-(ω,ω-dichloromethylene) norbornane **51** gave the following spectra: ^{1}H NMR 3.04 (s, 1H), 2.42 (s, 1H), 2.19 (ddd, 1H, J=16.5, J=3.9, J=2.1), 1.90 (dd, 1H, J=16.5, J=3.0), 1.61 (broad m, 2H), 1.17-1.47 (overlapping m's, 4H); ^{13}C NMR 144.8, 107.7, 44.1, 39.6, 39.5, 36.8, 27.5, 27.2; FTIR 2971(s), 2885(w), 1646(w), 1447(w), 157(92), 143(11), 141(35), 124(18), 122(29), 113(73), 111(40), 80(92), 79(50), 77(100); MS 180(4), 178(28), 176(43), 150(11), 149(54), 148(18), 147(82), 143(10), 141(33), 113(68), 105(54), 99(22), 77(100), 67(48), 51(58).

Attempted silylation of 2-(ω,ω-dichloromethylene)norbornane **51**

Method A: In an oven-dried, argon flushed 5 mL round-bottom flask equipped with a magnetic stirred and argon balloon a solution of 176 mg 2-(ω,ω-dichloromethylene)norbornane **51** (1 mmol) in 2 mL ethyl ether was treated with 0.65 mL 1.7 M *tert*-butyl lithium (1.1 mmol-Aldrich, in hexanes) at -115 °C. The solution was stirred for 30 minutes and then quenched with 0.25 mL trimethylchlorosilane (2 mmol) at -115 °C. After stirring 1.5 hours the solution was allowed to warm to room temperature. Analysis by GC/FTIR/MS showed starting material and what may be a dimer of the double-dechlorinated starting material but none of the desired product. Spectral data for the possible dimer **53** are: MS 213 (21), 212 (M^{+}, 100), 183 (71), 155 (79), 128 (65), 115 (87), 106 (6), 105 (30), 91 (89); FTIR 2968(s), 2881(m), 1441(w), 1301(w), 1277(w), 1159(w), 942(w).

Method B: A mixture of 176 mg 2-(ω,ω-dichloro-methylene)norbornane **51** (1 mmol), 23 mg magnesium (1 mmol-Aldrich, turnings), and 540 mg trimethylchlorosilane (5 mmol-Aldrich, 98%) in 5 mL tetrahydrofuran (Fisher,

ACS, distilled from calcium hydride) was refluxed for 15 hours. Analysis by GC/FTIR/MS showed only unreacted starting material.

Method C: A solution of 176 mg 2-(ω,ω-dichloromethylene)norbornane **51** (1 mmol), 270 mg trichlorosilane (2 mmol-Petrarch), and a trace of chloroplatinic acid (sufficient to faintly color the solution) in 1 mL benzene (Fisher, ACS) was stirred at room temperature for 24 hours. Analysis by GC/FTIR/MS showed no evidence of reaction.

Attempts to trap 2-vinylidene norbornane with cyclohexene **53**

Method A: A solution of 88 mg 2-(dichloromethylene)norbornane (0.5 mmol) and 200 mg cyclohexene (2.5 mmol) in 5 mL ethyl ether (Fisher, anhydrous distilled from lithium aluminum hydride) was cooled to -78 °C and treated with 0.7 mL 1.42 M *n*-butyl lithium (0.5 mmol-Aldrich, in hexanes). The solution was allowed to warm to room temperature. Analysis by GC/FTIR/MS showed no trapping product, coupling products were apparent.

Method B: The reaction described in Method A was repeated with toluene (Fisher, HPLC grade dried over anhydrous calcium chloride) rather than ether. GC/FTIR/MS analysis showed only starting material. A second equivalent of *n*-butyl lithium still gave none of the trapped adduct.

Method C: The reaction described in Method A was repeated with tetrahydrofuran (Fisher, ACS distilled from calcium hydride) rather than ether, and 1 equivalent of *tert*-butyl lithium (Aldrich, 1.6 M in hexanes) rather than *n*-butyl lithium. Still, only coupling was observed.

Synthesis of bis(trimethylsilyl)dichloromethane 53[40]

An oven-dried, argon flushed, 100 mL round-bottom flask, equipped with a magnetic stirring bar, condensor, and oil bath, was charged with 6.5 g trimethylchlorosilane (60 mmol-Aldrich, 98%), 1.38 g magnesium (60 mmol-Fisher, turnings), 60 mg zinc (Aldrich, dust), and 40 mL tetrahydrofuran (Fisher, ACS, distilled from calcium hydride). A solution of 4.32 g trimethylchlorosilane (40 mmol) and 3.08 g carbon tetrachloride (20 mmol-Fisher, ACS) was added slowly, *via* syringe. When ca. one fourth of the solution was added, and no reaction was apparent, the reaction mixture was brought to reflux and salts appeared before the addition was continued. The mixture was refluxed an additional 3 hours after the addition was complete. The reaction mixture was cooled to 0 °C and quenched by addition of saturated ammonium chloride. The mixture was diluted with an equal volume of pentane and washed with water. The pentane solution was dried over anhydrous sodium sulfate and then the solvents stripped, leaving 1.84 g amber-clear liquid which was a mixture of, predominantly, *bis*(trimethylsilyl)dichloromethane and tris(trimethylsilyl)methane in a 1.6:1 ratio (by GC). The compounds were separated by preparative GC. Bis(trimethylsilyl)dichloromethane **53** gave the following spectra: ^{1}H NMR 0.21 (s); ^{13}C NMR 74.6, -2.3 (q, J_{C-H}=119.7); FTIR 2968(w), 2911(w), 1262(m), 873(s); MS 230(0.6), 228(0.9), 115(1), 113(1.6), 105(23), 95(13), 93(37), 85(41), 73(100). Tris(trimethylsilyl)methane gave the following spectra: ^{1}H NMR 0.06 (s, 27H), -0.82 (s, 1H); ^{13}C NMR 3.3, 1.2; FTIR 2960(w), 2907(w), 1262(m), 1014(m), 853(s); MS 217(M^{+}-15, 100), 201(4), 129(36), 113(4), 99(3), 85(3), 73(49), 59(20).

Attempted Peterson reaction of bis(trimethylsilyl)dichloromethane **53** with norcamphor

Method A: In an oven-dried, argon flushed, 5 mL round-bottom flask equipped with a condensor and a magnetic stirrer 12 mg magnesium (0.5 mmol-Aldrich, ca. 20 mesh) and 2 mg zinc (Aldrich, ca. 20 mesh) were added to a solution of 76 mg norcamphor (0.7 mmol), and 80 mg bis(trimethylsilyl)dichloromethane **53** (0.35 mmol) in 1 mL tetrahydrofuran (Fisher, ACS, distilled from calcium hydride). When refluxing for 4 hours failed to produce any reaction, ca. 5 μL dibromoethane was added to initiate the reaction. After refluxing for 18 hour analysis by GC/FTIR/MS showed only starting materials.

Method B: In an oven-dried, argon flushed, round-bottom flask equipped with a condensor and magnetic stirrer 18 mg (0.78 mmol-Aldrich, ca. 20 mesh) and a few very small crystals of iodine were combined. The flask was heated to sublime the iodine onto the surface of the magnesium. After cooling to room temperature a solution of 76 mg norcamphor (0.7 mmol) and 80 mg **53** (0.35 mmol) in 1.5 mL tetrahydrofuran (Fisher, distilled from calcium hydride) was added to the flask. The reaction mixture was stirred at room temperature overnight. No reaction was apparent by GC/FTIR/MS analysis of the mixture. The reaction mixture was refluxed for 24 hours but still showed no sign of reaction.

Method C: A mixture of 50 mg magnesium (Aldrich, ca. 20 mesh) in 9 mL tetrahydrofuran (Fisher, ACS distilled from calcium hydride) was placed in an oven-dried, argon flushed, round-bottom flask equipped with a condensor

and magnetic stirrer. An aliuot of 20 μL dibromoethane was added to clean the surface of the magnesium. A solution of 220 mg **53** in 1 mL tetrahydrofuran was slowly added *via* syringe to the well stirred mixture, and the mixture was then stirred at room temperature for 1.5 hours. A dark gray color devleoped. GC analysis showed complete consumption of the dichloride, however, quenching of aliquots with acetone, hexylbromide, and deuterium oxide showed none of the expected quenching products. Only products arising from silane coupling, bis(trimethylsilyl)acetylene and tetrakis(trimethylsilyl)-ethylene, were evident. The coupling products were identified by MS and retention time comparison to authentic samples.

Method D: An oven-dried, argon flush, round-bottom flask equipped with a magnetic stirrer and balloon of argon was charged with 1.29 g mixture of bis(trimethylsilyl)dichloromethane **53** and tris(trimethylsilyl)methane **54** (1.3:1 - ca. 5.6:2.5 mmol, respectively) and 10 mL ethyl ether (Fisher, ACS, distilled from lithium aluminum hydride). The solution was cooled to -78 °C and treated with 3.2 mL 1.42 M *n*-butyl lithium (4.5 mmol-Aldrich, in hexanes) by slow syringe addition. After ca. 15 minutes GC analysis indicated complete consumption of the dichloride. A solution of 1.1 g norcamphor (10 mmol) in 2 mL ethyl ether was added at -78 °C. After warming to room temperature over a 1.5 hour period, GC/FTIR/MS showed only products derived from coupling of dichlorides.

Method E: In an oven-dried, argon flushed, round-bottom flask equipped with a magnetic stirrer and argon balloon, 220 mg bis(trimethylsilyl)dichlorosilane **53** (1 mmol) and 88 mg lithium bromide (1 mmol-Alpha, anhydrous) were dissolved in 10 mL tetrahydrofuran (Fisher,

distilled from calcium hydride) and then cooled to -114 °C. Slowly, *via* syringe, 0.85 mL 1.42 M *n*-butyl lithium (1.2 mmol-Aldrich, in hexanes) was added and allowed to react over a 30 minute period. A solution of 110 mg norcamphor (1 mmol) in 1.5 mL tetrahydrofuran was then added to the solution, still at -114 °C. The solution was allowed to warm to room temperature over a 3 hour period. Analysis by GC/FTIR/MS showed no reaction.

Method F: The reaction was set up as described in Method E except an equivalent of lithium bromide was added to the ketone solution. GC monitoring of the reaction mixture for 5 hours showed no change in the concentration of the dichloride. The mixture was allowed to warm to room temperature but still none of the dichloride was consumed.

Method G: The reaction described in method F was repeated using ethyl ether (distilled from lithium aluminum hydride) rather than tetrahydrofuran. No reaction was apparent.

Synthesis of bis(trimethylsilyl)methane 55[40]

In a 1 L round-bottom flask equipped with a condensor, 32 mL methylene chloride (0.54 mol-Fisher, ACS, dried over calcium chloride), 24.3 g magnesium (1.05 mol-Fisher, turnings), 190 mL trimethylchlorosilane (2.43 mol-Aldrich, 98%), and 450 mL tetrahydrofuran (Fisher, ACS distilled from calcium hydride) were combined and refluxed for 18 hours. The excess chlorosilane was removed by distillation and the mixture was then washed with 2-100 mL portions of water and once with 100 mL dilute hydrochloric acid. After drying over sodium sulfate the product was obtained by careful distillation through a 6 inch column packed with glass helices. The forerun

consisted of 4.45 g 61% bis(trimethylsilyl)methane **55**, the heart cut consisted of 4.8 g 95% **55**, and the third fraction 1.0 g 91% **55** for a total of 8.18 g **55** (9% yield). Bis(trimethylsilyl)methane **55** gave the following spectra: ^{1}H NMR: 0.088 (s, 1H), -0.026 (s, 9H); ^{13}C NMR: 1.93, -3.05; MS 145 (M^{+}-15), 129(7), 101(2), 99(2), 85(4), 73(84), 65(11), 59(21).

Attempted lithiation of bis(trimethylsilyl)methane **55**

Method A: A solution of 172 mg bis(trimethylsilyl)methane **55** (1 mmol) in 10 mL ethyl ether (Fisher, anhydrous distilled from lithium aluminum hydride) was placed in an oven-dried, argon flush, 25 mL round-bottom flask equipped with a magnetic stirrer and argon balloon. The solution was cooled to -78 °C and 0.65 mL 1.6 M *tert*-butyl lithium (Aldrich, in hexanes) was added over a 5 minute period. The flask was allowed to warm to room temperature and, at the same time, aliquots were periodically removed, quenched with trimethylchlorosilane (Aldrich, 98%) and checked by GC/FTIR/MS. Only *tert*-butyltrimethylsilane was formed. After no reaction of the bis(trimethylylsilyl)methane was evident after 18 hours, 250 μL tetramethylethylenediamine was added. Five hours later no lithiated product was evident; the starting material remained.

Method B: A solution of 112 mg potassium *tert*-butoxide (1 mmol-Aldrich) in 10 mL tetrahydrofuran (Fisher, ACS, distilled from calcium hydride) was treated with 0.63 mL 1.6 M *n*-butyl lithium (1 mmol-Aldrich, in hexanes). Slowly, *via* syringe, 162 mg bis(trimethyl)methane **55** (1 mmol)was added. Trimethylchlorosilane quenched aliquots showed by GC/FTIR/MS

analysis no reaction after 4 hours at room temperature. The solution was refluxed overnight but still failed to give evidence of any reaction.

Method C: At -78 °C a solution of 0.75 g bis(trimethylsilyl)methane **55** (4.6 mmol) and 0.543 g tetramethylethylenediamine (4.6 mmol-dried successively over 3Å molecular sieves), 2.75 mL 1.7 M *tert*-butyl lithium (Aldrich, in pentane). The reaction mixture was checked daily for 10 days by quenching alqiuots with trimethylchlorosilane. None of the bis(trimethylsilyl)methane **55** appeared to have been lithiated. Only starting material and *tert*-butyl trimethylsilane were observed.

Synthesis of trimethylsilyldiazomethane **60**[44]

A 100 mL round-bottom flask equipped with a stirring bar, condensor, and dropping funnel was flushed with argon and charged with 2.7 g magnesium turnings (117 mmol) and 8 mL ethyl ether (Fisher, anhydrous) and was then heated for 15 minutes. Chloromethyltrimethylsilane (9.1 g-74 mmol-Petrach, 98%) in 20 mL ethyl ether was added *via* the dropping funnel, first ca. 2 mL at once and stirred until the reaction became cloudy and then dropwise over a 45 minute period. The exothermicity of the reaction was sufficient to maintain reflux for the addition period. The reaction mixture was refluxed an additional 1 hour.

Meanwhile, a 250 mL round-bottom flask fitted with a mechanical stirrer and a thermometer was flushed with argon and charged with 22.8 g diphenylphosphoryl azide (83 mmol-Lancaster, 98%) and 88 mL ethyl ether. The solution was cooled to -10 °C and the Grignard reagent (*vide supra*) was added at such a rate that the temperature of the reaction mixture did not

exceed 0 °C. The reaction mixture was stirred at 0 °C (bath temperature) for an additional 2 hours and the bath then allowed to melt and the solution warm to room temperature.

After 18 hours at room temperature the mixture was cooled to -10 °C and 9 mL water was added *via* syringe over a 30 minute period, being careful that the mixture's temperature did not exceed 0 °C. The milky white suspension developed a yellow-green color during the course of the addition. The salts were vacuum filtered through Celite and washed with three 20 mL portions of ethyl ether.

The filtrate was washed with two 10 mL portions of water and dried over sodium sulfate and then trap-to-trap distilled at ca. 2 mmHg and 60 °C. After diluting with 25 mL hexane the solution was again dried over sodium sulfate. The solution was slowly distilled through a six inch column packed with glass helices until the head temperature reached 68 °C and the bath temperature reached 85 °C. The still pot contained ca. 15 mL deep yellow-green solution.

An aliquot of 0.83 mL of the solution was spiked with 46 mg toluene and the concentration of the azide determined by the ratio of the integration of the azide proton to the methyl protons of the toluene. The concentration was determined to be 3.79 μ (ca. 79% yield). The product **60** gave the following spectra: ^{1}H NMR 2.56 (s, 1H), 0.12 (s, 1H); ^{13}C NMR 1.27-0.99; FTIR 2966(w), 2071(s), 1262(m), 851(m); MS 115(4), 114(M^+, 42), 99(39), 85(6), 73(22), 58(100).

Synthesis of bis(trimethylsilyl)diazomethane **59**[45]

In an oven-dried, argon flushed 100 mL round-bottom flask equipped with a magnetic stirrer and a balloon of argon, 6 mL 2.79 M

trimethylsilyldiazomethane **60** in hexane (17.8 mmol) was dissolved in 35 mL tetrahydrofuran (18.5 mmol Aldrich, in hexanes) added *via* motor driven syringe over a 45 minute period. The solution was stirred at -78 °C for an additional 1 hour and 5 mL trimethylchlorosilane (38 mmol-Aldrich 98%) was added *via* syringe over a 30 minute period. The mixture was allowed to warm to room temperature over a 2 hour period during which time copious amounts of salt formed. The mixture was stirred at room temperature for 4 hours. The solvent was stripped by rotary evaporation and replaced with hexane and then the precipitated salts removed by vacuum filtration through magnesium sulfate over a glass fit. The hexane was removed by vacuum distillation to 25 °C and 0.2 mmHg leaving 4.36 g of clear-yellow liquid which was a 2.3:1 mixture of the bis(trimethylsilyl)diazo- and bis(trimethylsilyl)diazarene-methane. They were used without further purification. An analytical sample of bis(trimethylsilyl)diazomethane was purified by preparative GC (6 foot x 1/4 inch glass column with 15% SE-30 on CW). It gave the following spectra: ^{1}H NMR 0.132(s); ^{13}C NMR 123.9, -0.85; FTIR 2964(w), 2050(s), 1261(m), 929(m), 844(m); MS 187(2), 186(M^+, 15), 143(39), 85(13), 83(28), 73(100), 59(31). Bis(trimethylsilyl)diazarenemethane gave the following spectra: ^{1}H NMR 0.216(s); ^{13}C NMR 132.2, -0.52; FTIR 2967(w), 2199s), 1265(w), 904(s), 852(s); MS 186 (M^+, 5), 171(100), 73(17).

Photolysis of bis(trimethylsilyl)diazomethane 59 and norcamphor

A solution of 0.903 g bis(trimethylsilyl)diazomethane **59** (5 mmol) and 0.550 g norcamphor (5 mmol) in 10 mL hexane (Fisher, HPLC grade) was placed in a quartz tube and degassed by bubbling argon through the solution.

The tube was capped with a septum an the irradiated for 1 hour (254 nm). The diazomethane was consumed. Some norcamphor remained. The major product, norbornylsilyl ether **62a**, was isolated by preparative GC. It gave the following spectra: ^{1}H NMR 6.28 (dd, 2H, J=5.6, J=18.4), 4.60 (dd, 1H, J=0.9, J=3.0) 2.71 (s, 1H), 2.50 (s, 1H), 1.6-1.8 (m, 4H), 1.4-1.5 (m, 2H), 1.1-1.2 (m, 2H), 0.01 (s, 6H), -0.01 (s, 9H). ^{13}C NMR 161.2, 140.8, 104.9, 46.9, 45.5, 40.9, 27.8, 24.5, 24.5, -0.7, -1.07; FTIR 2969(s), 2880(w), 1614(m), 1332(m), 1260(m), 1233(m), 896(w), 838(s). MS 268 (M^+, 39), 253(48), 240(100), 225(31), 167(81), 159(32), 147(73), 140(30), 131(23), 85(63), 75(35), 73(97).

Photolysis of bis(trimethylsilyl)diazomethane **59** and 2-adamantanone

Method A: The reaction was set up and run just as the preceeding reaction except 0.750 g adamantanone was used rather than norcamphor. The adamantylsilyl ether **62b** gave the following spectra: ^{1}H NMR 6.30 (dd, 2H, J=5.4, J=19.2), 3.77 (s, 1H), 2.13 (d, 2H, J=12), 1.70 (m, 8H), 1.39 (d, 2H, J=12), 0.13 (s, 6H), 0.08 (s, 9H); ^{13}C NMR 154.3, 140.5, 75.2, 37.8, 36.6, 35.1, 31.3, 27.6, 27.2, -0.3, -0.5; FTIR 2916(s), 2862(w), 1257(w), 1102(m), 1070(m), 1035(w), 859(m); MS 309 (6), 308 (M^+, 21), 293 (20), 235 (46), 209 (26), 159 (23), 147 (55), 135(89), 107 (8), 93 (18), 91 (12), 79 (20), 75 (100), 73 (46).

Method B: A quartz tube was charged with 5 mL benzene (Fisher, ACS-dried over 3Å molecular sieves), 0.55 g bis(trimethylsilyl)diazomethane **59**, (0.3 mmol), and 0.44 g 2-adamantanone (0.3 mmol Aldrich-99%). The solution was degassed by freezing and thawing. The tube was irradiated (254 mm) for 4 hours. The walls of the tube were coated with a yellow residue. GC/MS analysis showed most of the bis(trimethylsilyl)diazomethane **59** was

consumed, most of the ketone remained, and a small amount of the adamantylsilyl ether **62b** described in method A. The product was not quantitated.

Photolysis of bis(trimethylsilyl)diazomethane 59 and benzaldehyde

A quartz NMR tube was charged with 110 mg bis(trimethylsilyl)diazomethane **59** (0.59 mmol) and 1 mL d_6-benzene and 65 mg benzaldehyde (0.61 mmol) was added. The tube was irradiated for one hour. GC showed no obvious reaction. After an additional hour of irradiation GC still showed only starting material. ^{1}H NMR showed no peaks which could be assigned to an epoxide. Only the aldehydic and aromatic proton and several peaks near 0 ppm. After an additional 5 hours no epoxide formation was evident by NMR analysis.

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GENERAL SUMMARY

It has been demonstrated that bicyclo[2.2.2]oct-1-ene **1** was generated in the gas-phase and that the predominant fate of the strained olefin in 2 + 2 cycloaddition. The crystal structure of the head-to-head dimer supports the view that the transient olefin is non-dipolar.

Products of flash vacuum pyrolytic generation of 2-vinylidene norbornane **2** shows evidence for the ring contraction of the alkylidene carbene **2**. This, coupled with force field calculation, suggests strain is not the only important factor regulating ring contraction and ring expansion reaction of bicyclic alkylidene carbenes.

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