*Chem. Rev.* **1989**, *89*, 975–983

# Small-Ring Propellanes

KENNETH B. WIBERG

*Department of Chemistry, Yale University, New Haven, Connecticut 06511*

*Received November 17, 1988 (Revised Manuscript Received April 4, 1989)*

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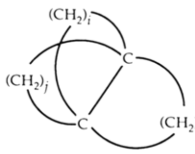
## *1. Introduction*

The name propellane was proposed by Ginsburg for compounds having three nonzero bridges and one zero bridge between a pair of bridgehead carbons. In an uncomplicated case, an [*i.j.k*]propellane would have the systematic name tricyclo[$i.j.k.0^{1,i+2}$]($i+j+k+2$)ane. Propellanes have been the subject of several reviews by Ginsburg which cover the literature through part of 1984.[1]

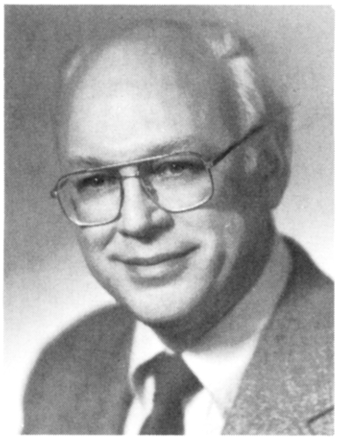


The small-ring propellanes have one or more three- or four-membered rings. Many of them have the interesting characteristic of having an "inverted" tetrahedral geometry at the bridgehead carbons. This is readily seen for the case of [1.1.1]propellane (1).

1

The chemistry of small-ring propellanes was reviewed by Wiberg in 1984.[2] In that review the literature was covered through 1983. The present review will briefly summarize some of the earlier results and then concentrate on the results that have been reported over the past few years.

## *2. [1.1.1]Propellane*

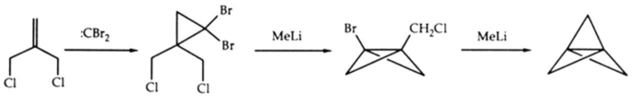


Kenneth B. Wiberg received his B.S. from the Massachusetts Institute of Technology in 1948 and the Ph.D. from Columbia University in 1950, where he studied under William Doering. He joined the faculty at the University of Washington in 1950, was visiting professor at Harvard in 1957–1958, and joined the faculty of Yale University in 1962, where he is the Whitehead Professor of Chemistry. His research interests are in the areas of small-ring chemistry, thermochemistry, spectroscopy, and the use of theoretical methods to explore problems in organic chemistry.

[1.1.1]Propellane is the smallest and possibly the most interesting of the small-ring propellanes. The ease of formation and relatively low reactivity were first predicted theoretically and then confirmed via its preparation from 1,3-dibromobicyclo[1.1.1]pentane:[3]

2 1

The dibromide **2** is not readily accessible. Szeimies recognized that the thermochemistry of the formation of **1** from a bicyclobutane is about the same as that from **2**. This led to a simple preparation from readily available reagents:[4]



This procedure makes **1** one of the more easily obtained of small-ring compounds. It has also been possible to obtain **1** via a carbene pathway.[5]

1

It seems appropriate first to describe the theoretical studies of **1** since its ease of formation, stability, structure, vibrational spectra, photoelectron spectra, and enthalpy of formation were all predicted prior to its preparation.[6,7] It appears to be the first polyatomic molecule for which this was done, and all of the theoretical predictions were satisfactorily confirmed by subsequent experimental studies.[7–10]

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## A. Theoretical Studies

The first theoretical studies were reported by Newton and Schulman (4-31G)[11] and by Stohrer and Hoffmann (EHT).[12] Both investigations led to the conclusion that 1 should be more stable than the corresponding stretched diradical, but neither one concluded that the compound would be capable of existence. Later calculations by Wiberg dealing with the energetics of the hydrogenolysis of the central bonds in a series of propellanes led to the at first surprising conclusion that 1 should be as easily prepared from a 1,3-dihalobicyclo[1.1.1]pentane as cyclopropane is prepared from a 1,3-dihalopropane.[6] It was then recognized that this resulted from the high strain energy of the bicyclo[1.1.1]pentane ring system, allowing 1 to be formed with a relatively small increase in strain energy.

The nature of the central bond in 1 has been the subject of many studies.[6,7,11-24] The observation of Chackrabarti et al. that, based on an X-ray crystallographic study, the central bond of a [3.1.1]propellane derivative had essentially no deformation density[13] has led to a common misconception that the central bond has no charge density. On the contrary, the charge density is 80% that of the $C_2$–$C_3$ bond in *n*-butane.[14]

An analysis of the charge density distribution in 1 showed that there was a normal bond critical point for the central bond.[14] In addition, there were three ring critical points associated with the three cyclopropane rings, and they were close to the bond critical point. Therefore, the charge density at the midpoint of the bond is more spread out than normal, leading to a "fat" bond. Two unusual features of the charge distribution were the high local charge density near the bridgehead carbons[20,25] and the bond path angles at the methylene group. The high charge density is expected for this type of structure since there are no bonds in a large volume of space that must be occupied by the backsides of the bonding orbitals.

Most cyclopropanes have C–C–C bond path angles at the methylene groups of about 78° corresponding to the bent bonds originally suggested by Coulson and Moffitt.[26] However, with 1, the bond path angle is slightly smaller than the conventional angle.[14] The only other unusual property of the methylene group is the large difference in the out-of-plane component of the $^{13}C$ chemical shift with respect to bicyclobutane and cyclopropane.[10] The 178 ppm change in this component through the series is unprecedented and may in some way be related to the changes in bond path angles.

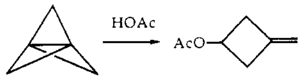
Perhaps the best evidence for an energetically favorable $C_1$–$C_3$ bond is found in the work of Feller and Davidson.[23] Their calculations led to a bridgehead C–H bond dissociation energy of 106 kcal/mol for bicyclo[1.1.1]pentane, in good agreement with expectations for a hydrogen bonded to a stained carbon. However, the second bridgehead C–H bond had a dissociation energy of only 47 kcal/mol. The difference, 59 kcal/mol, must be attributed to a $C_1$–$C_3$ interaction, and considering its strength, it may reasonably be called a bond. It has 70% of the strength of a normal C–C bond (84 kcal/mol). The GVB calculations of Messmer and Schultz also are best interpreted in terms of a $C_1$–$C_3$ bond.[22]

The calculations of Jackson and Allen using their "$\sigma$-bridged-$\pi$" model suggested that the $C_1$–$C_3$ bonding interaction was not primarily concerned with the highest occupied MO, despite what one might have guessed on a simple hybridization model.[15] A similar suggestion was provided by the photoelectron spectrum in which the lowest energy ionization process was found not to lead to a significant change in structure.[8] However, it also is possible that the ring structure is so rigid that little change in structure is possible on going to the radical cation.

The effect of replacing one or more of the carbons in 1 by heteroatoms has been explored theoretically, but these predictions have not as yet been subject to experimental tests.[15,17,24] Theoretical studies of the effect of adding additional C–C bonds also have been reported.[27] These studies lie outside the focus of this review. Although ab initio MO theory has been the major tool in examining these compounds, they also have been studied by semiempirical MO theory[28] and molecular mechanics.[29] In the use of the latter, the main problem is that the bending potential functions for normal compounds cannot be expected to apply for large deviations that result in rehybridization.

## B. Reactions of [1.1.1]Propellane

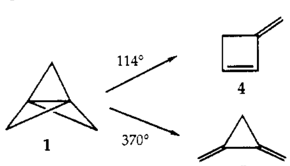
The first reaction of 1 that was studied was its reaction with acetic acid leading to ring opening:[3]



1 3

The initial proton addition step could lead to either the 1-bicyclo[1.1.1]pentyl or the 1-bicyclo[1.1.0]butanemethyl cation. Both have been studied and are known to rearrange to the 3-methylenecyclobutyl cation,[30] which would then form the observed acetate, 3. The importance of this reaction is that the enthalpy of reaction has been measured,[7] and the enthalpy of formation of 3 has been determined.[31] A combination of these data gives $\Delta H_f$ = 85 kcal/mol for 1, which may be compared with the theoretically deduced value of 92 kcal/mol.[32] The strain energy of 1 is 98 kcal/mol.

The second reaction to be studied is the thermolysis.[3] Using a stirred flow reactor at 114 °C, Wiberg and Walker found that the product was methylenecyclobutane (4). Subsequently, Belzner and Szeimies reported that thermolysis at 370 °C gave 1,2-dimethylenecyclopropane (5).[33] The reason for the difference in results is not understood. One of the reactions may have been subject to inadvertent catalysis, or there may be two reaction channels having significantly different entropies of activation. This question continues to be studied.



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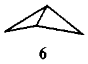
A reason for the interest in the reactions of 1 can be found in a comparison with bicyclo[1.1.0]butane (6) and bicyclo[2.1.0]pentane (7).[25] Most of the reactions of



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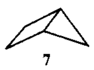

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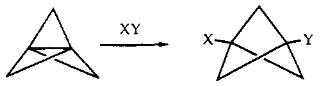
these compounds involve the cleavage of the central bond. If this type of reaction had a late transition state, bicyclopentane should be the more reactive of the three because both small rings would be lost, leading to the largest strain energy relief. These reactions might also involve initial charge transfer or some other process that responds to the differences in HOMO energies. In this case, bicyclobutane should be the more reactive because it has the lowest ionization potential.[8] Finally, the reaction might respond to the charge density near the bridgehead carbon. Here, **1** should be the more reactive of the three.[25] It can be seen that studies of the relative reactivities of **1**, **6**, and **7** for a given process may yield useful information on the nature of the activated complex.

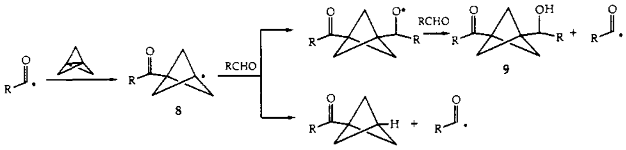
## C. Free Radical Additions

In a study of free radical additions, Wiberg, Waddell, and Laidig found that **1** was about 8 times as reactive as **6** and that **7** was unreactive.[25] These free radical reactions lead to a wide variety of 1,3-disubstituted bicyclo[1.1.1]pentanes:



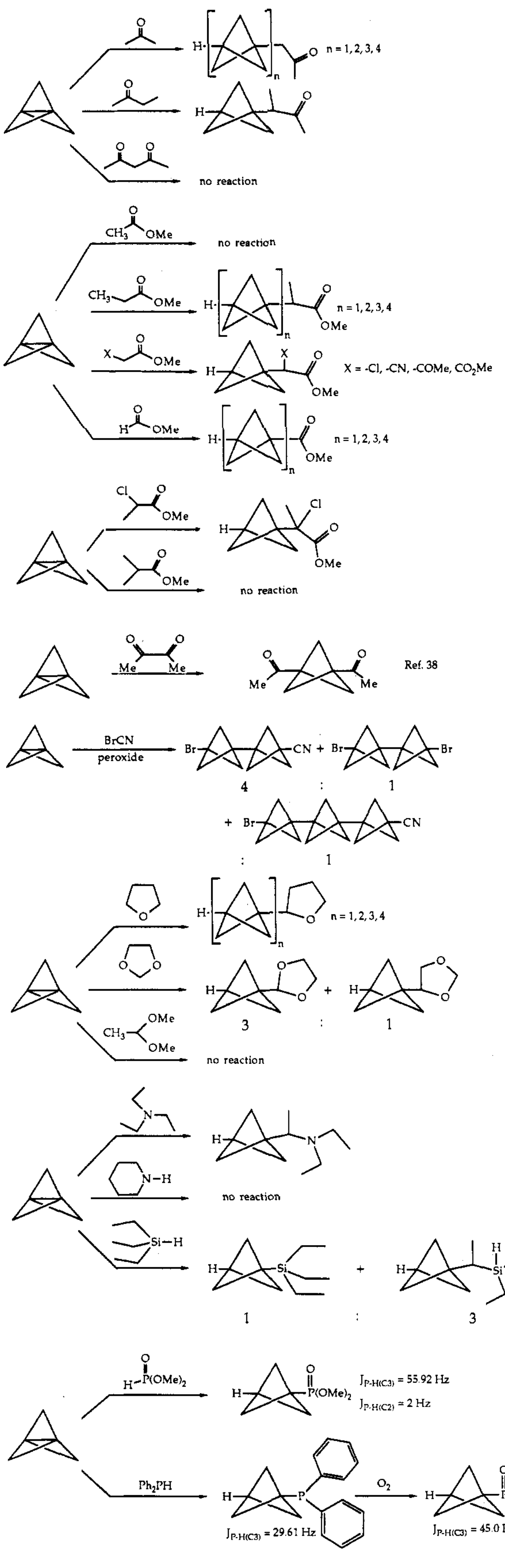
Reagents that added spontaneously included $CCl_4$, $BrCCl_3$, $I_2$, PhSH, PhSSPh, PhSeSePh, and *t*-BuOCl.[4,25,34-36] Although the reaction of **1** with iodine gives only the 1,3-dihalide, the light-catalyzed reactions of **1** with $PhICl_2$ and with bromine have been reported to give both 1,3-dihalides and ring-opened tetrahalides.[37]

In other cases, it was found necessary to initiate the free radical additions.[25,34-36] Examples of these reactions are shown in Scheme I. Some of them are of special interest. The addition of aldehydes may give either 1:1 or 2:1 adducts. The latter are formed when the initially formed bridgehead radical (**8**) adds to the carbonyl group of an aldehyde in preference to the normal reaction of carbon radicals, hydrogen abstraction:

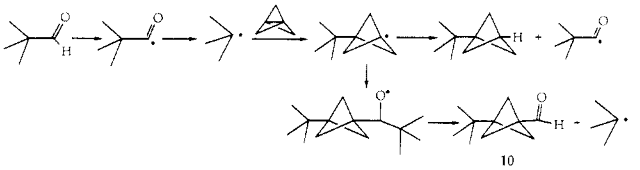


With acetaldehyde only the 2:1 adduct (**9**) was formed. This reaction leads to differentiated carbon functions at the bridgehead carbons. The adduct may be oxidized with hypoiodite to bicyclo[1.1.1]pentane-1,3-dicarboxylic acid, presumably via 1,3-diacetylbicyclo[1.1.1]pentane as an intermediate. The latter may also be formed directly via addition of diacetyl to **1**.[38] This procedure provides a convenient route to the diacid, which when prepared via a more difficult route was the precursor for the original preparation of **1**! Benzaldehyde undergoes the same type of addition, but the more sterically hindered *n*-butyraldehyde gives both 1:1 and 2:1 adducts.

**SCHEME I. Catalyzed Free Radical Addition Reactions**[4,25,35,36,38]

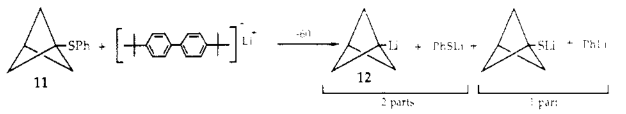


α-Branching in the aldehyde would stabilize the radical formed by decarbonylation of the chain-carrying acyl radical, and with isobutyraldehyde this reaction is competitive with chain propagation. As a result, part of the product is formed via the addition of the isopropyl radical. With pivaldehyde, decarbonylation is complete, and *tert*-butyl is the chain-carrying radical. The intermediate that would form the 2:1 adduct also may lose a *tert*-butyl radical, leading to the aldehyde **10** as one of the products:



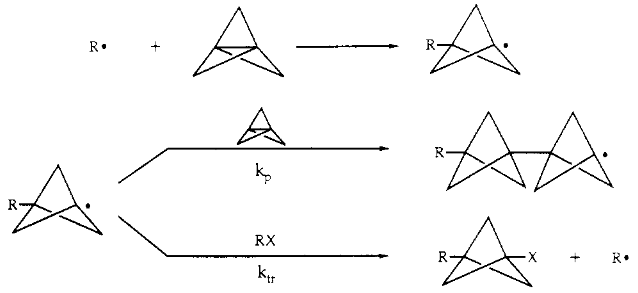
The addition of diphenylphosphine gave a 1:1 adduct having a long-range NMR coupling between phosphorus and the carbon at the other bridgehead position of 30 Hz,[34,35] which is unusually large.[39] Large long-range coupling constants have frequently been observed with the bicyclo[1.1.1]pentane ring system.[40]

The phenylthiol addition product (**11**) was useful in that it will react with the radical anion derived from 4,4′-di-*tert*-butylbiphenyl[41] to give the bridgehead anion (**12**).[42] This, in turn allowed the preparation of a wide variety of 1-substituted bicyclo[1.1.1]pentanes.[34,42] The set of addition reactions now make a wide variety of 1- and 1,3-disubstituted bicyclo[1.1.1]pentanes readily available.



## D. Oligomers and Polymers Derived from [1.1.1]Propellanes

Whereas many of the free radical chain addition reactions of [1.1.1]propellane yield 1:1 adducts, others lead to oligomers. A number of examples are given in Scheme I. Hence, the critical quantity is the chain transfer constant. Consider the addition of RX, where R is the chain-carrying radical:



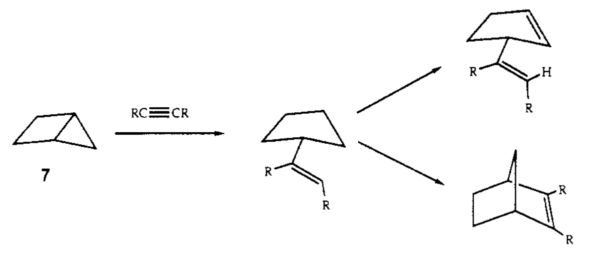
The ratio of $k_{tr}$[RX] to $k_p$[1] will control the ratio of 1:1 adduct to oligomer. Here, $k_{tr}$ is known as the chain transfer constant and $k_p$ is the chain propagation constant. It can be see that the degree of oligomer formation is controlled both by the $k_{tr}/k_p$ ratio and by the 1:RX ratio. High concentrations of 1 will favor the formation of oligomers.

The chain transfer constant is often affected by changes in structure. The addition of esters to 1 (Scheme I) provides one example. Here, methyl propionate gave the 1:1 adduct along with a series of oligomers. The use of an ester from which a hydrogen is more easily abstracted (i.e., a smaller C–H bond dissociation energy) led only to 1:1 adducts. The addition of ketones provides other similar examples of the effect of $\alpha$-branching on the course of the reaction.

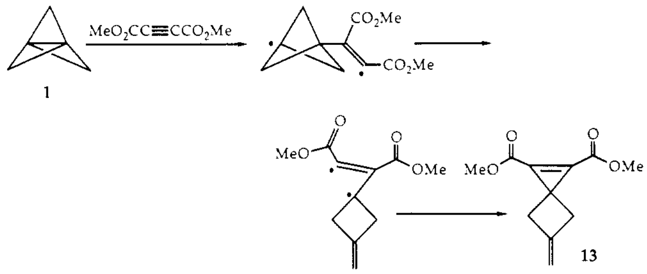
The oligomers derived from 1 have been studied by Michl et al. as building blocks for the formation of molecular networks with well-defined geometries.[35,43,44] The bridgehead–bridgehead bond lengths in the oligomers were found to be unusually short, in good accord with the expectation based on the hybridization of the bridgehead carbons.[36,43] Polymers derived from a bridged [1.1.1]propellane have been formed via anionic polymerization using *tert*-butyllithium.[45] Polymers derived from the parent [1.1.1]propellane were obtained both via free radical and anionic polymerization.[35] Copolymers of 1 with vinyl monomers also have been prepared.[46]

## E. Reaction with Electron-Deficient Alkenes and Alkynes

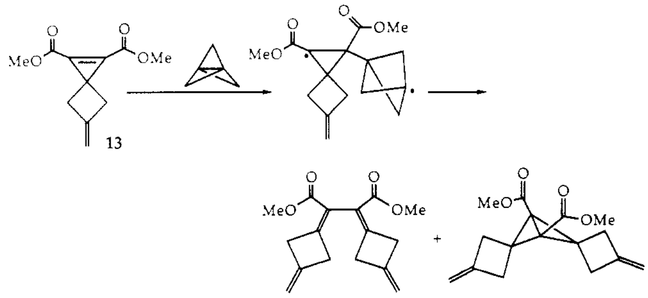
Many small-ring compounds undergo reaction with electron-deficient alkenes and alkynes. Two types of reaction have been observed, an ene reaction and a cycloaddition. This may be illustrated with bicyclo[2.1.0]pentane (**7**):[47]



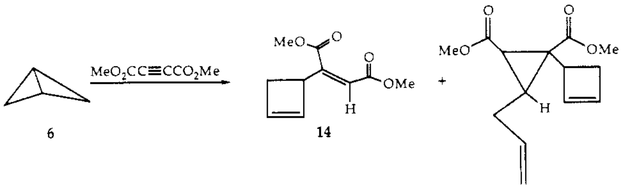
However, with 1, these reactions are not possible, and instead ring cleavage occurs after the initial diradical is formed:[48]



A similar type of reaction was first observed with a [3.2.1]propellane.[49] The cycloproprene (**13**) formed in this way also reacts with 1, leading to two 2:1 adducts:

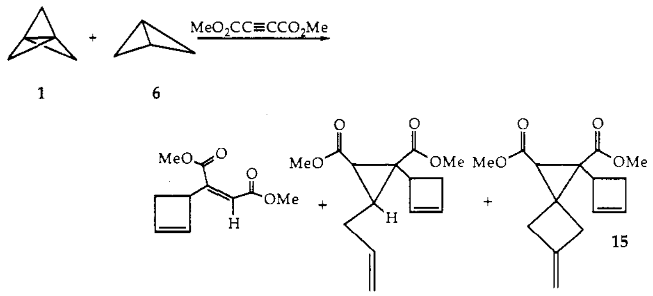


Bicyclobutane (**6**) was found to be more reactive than 1 toward dimethyl acetylenedicarboxylate, giving the ene product (**14**) along with a second compound that was presumably formed from an intermediate cyclopropene.[48] The latter is probably formed in the same fashion as that from 1. The ratio of the two types of



products was solvent dependent, with benzene and cyclohexane giving only the ene product and methanol giving about equal amounts of the two products.

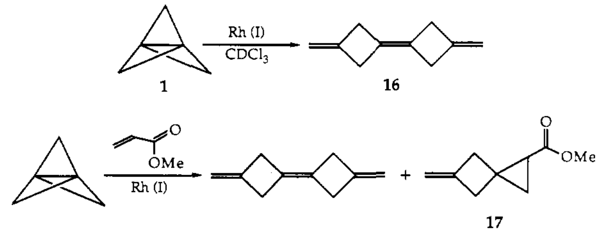
When a competition reaction between 1 and 6 was carried out, the intermediate cyclopropene derived from 1 reacted exclusively with 6 to give 15.



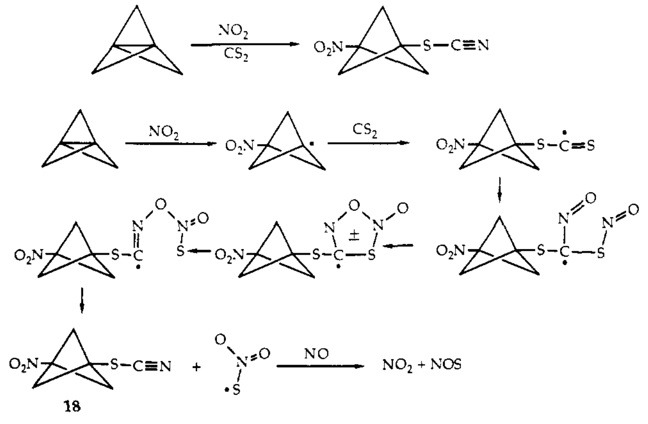
The reaction of 1 with a number of other electron-deficient double and triple bonds has been studied.[48] The reagents include dicyanoacetylene, tetracyanoethylene, and dichlorodicyanoquinone, and the reactions proceeded in essentially the same fashion as above. However, whereas bicyclobutane (6) reacted with fumaronitrile, 1 did not. The contrast in relative reactivity of 1 and 6 between the free radical additions and the reactions discussed above is worth noting.

## F. Other Reactions

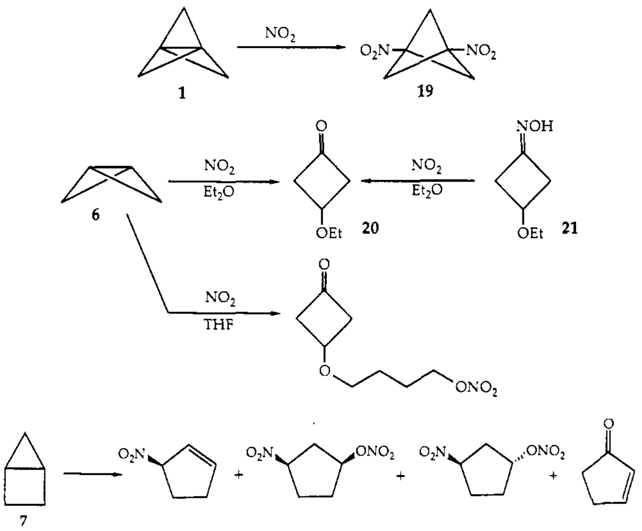
Metal-catalyzed reactions of 1 have so far not given monomeric products, but rather the dimer (16) is the major product. In the case of Rh(I) catalysis, 16 is presumably formed via a metallocarbene intermediate.[34] In support of this assumption, when the reaction was carried out in the presence of methyl acrylate, some of the carbene addition product (17) was found.



The reaction of 1 with nitrogen oxides revealed some interesting chemistry.[34] Treatment of 1 with NO in carbon disulfide gave 3-nitro-1-thiocyanobicyclo[1.1.1]pentane (18). In analogy with the reaction of NO with alkenes,[50] the reaction is probably initiated by $NO_2$, which is readily formed from NO by air oxidation. Reaction of the initial radical with carbon disulfide followed by further reaction with NO would give the observed product and regenerate $NO_2$ to carry the chain.

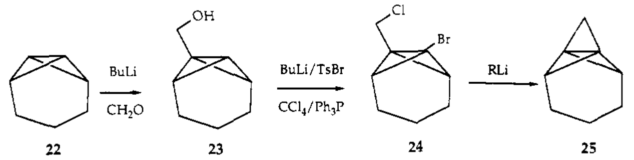


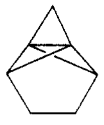
The reaction of 1 with $NO_2$ proceeded satisfactorily in ether and gave 1,3-dinitrobicyclo[1.1.1]pentane (19).[34] It is interesting to note that the reactions of bicyclobutane (6) and of bicyclo[2.1.0]pentane (7) proceeded via different routes. The reaction with 6 must involve cationic intermediates since only these species would be capable of cleaving ether to give the observed products. The oxime, 21, would be a reasonable intermediate, and it was found to give 3-ethoxycyclobutanone (20) on reaction with $NO_2$. The reaction of 7 also probably involves cationic intermediates. At first, one might think that the addition to 1 could not involve the bridgehead cation since 1-bicyclo[1.1.1]pentyl cation is known to readily undergo ring opening to 3-methylenecyclobutyl cation.[30] However, with a nitro group at the 3-position, the cation is much less likely to undergo ring cleavage and could reasonably be an intermediate.



### 3. Bridged [1.1.1]Propellanes

Szeimies et al.[5,51] have made good use of the acidity of the bridgehead protons of bicyclobutanes in developing procedures for the preparation of bridged [1.1.1]propellanes. This may be illustrated with "Moore's" hydrocarbon (22), which may be converted to its anion with butyllithium. A reaction with formaldehyde gave the alcohol (23), which on further treatment with butyllithium followed by tosyl bromide gave the bromo alcohol. It could be converted to the chloro bromide (24) with carbon tetrachloride and triphenylphosphine, and a final ring closure with methyllithium gave the bridged propellane, 25. Related compounds prepared by this method include 26 and 27. It also was possible to prepare 26 directly from the corresponding dilithiated bridged bicyclobutane via reaction with chloroiodomethane.





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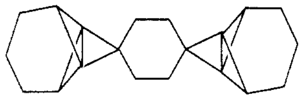

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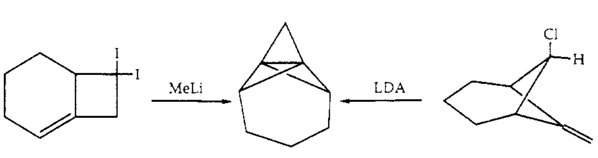
Another procedure for the preparation of the bridged propellanes makes use of the intramolecular addition of a carbene to a double bond. Two examples of the formation of 25 via this route are[52]



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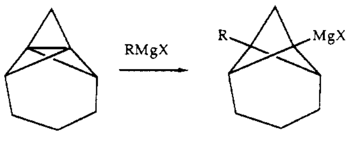
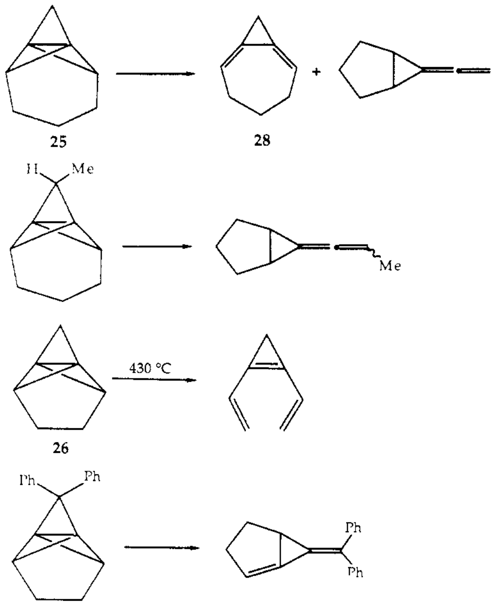
The structures of several of these compounds have been determined by X-ray crystallography, and the central bond lengths were found to lie in the range 1.577–1.586 Å,[5] slightly shorter than that for 1 (1.595 Å).[9]

The development of these convenient synthetic entries makes the compounds readily available. The bridged propellanes behave in much the same fashion as the parent hydrocarbon, 1.[52] For example, they add a variety of reagents such as diphenyl disulfide.[5] One of the more interesting and potentially useful of these reactions is that with Grignard reagents. The reaction proceeds slowly in boiling ether and leads to the cleavage of the central bond with the formation of a new Grignard reagent.[5] The latter reacts with the usual range of reagents, allowing the preparation of a variety of bridged bicyclo[1.1.1]pentane derivatives. It is interesting to note that the new Grignard reagent does not add to the reactant at an appreciable rate, thus minimizing the formation of dimers and oligomers.



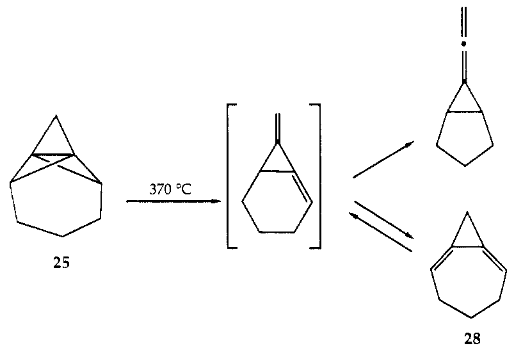
26

The thermal reactions also have been studied. Thermolysis of 25 at elevated temperatures results in ring cleavage, giving the diene, 28.[5]



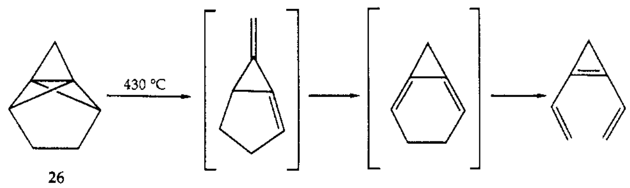
25 28 26

The direct cleavage in the fashion observed with bicyclobutane is not likely since it is orbital symmetry forbidden.[53] Rather, it is thought to proceed via the 2s + 2a cycloreversion shown below:



25 28

The cleavage of 26 is believed to proceed in a similar fashion:

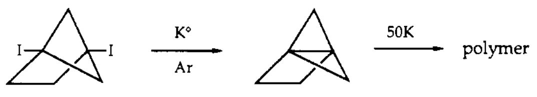


26

All of these reactions proceed with retention of the central propellane bond.

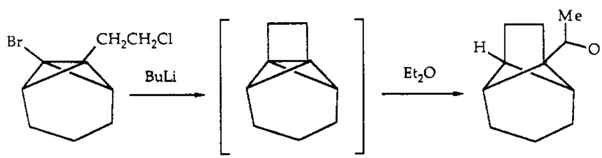
### 4. [m.1.1]Propellanes

Reductive dehalogenation of 1,4-diiodobicyclo[2.1.1]hexane with butyllithium appears to proceed via formation of [2.1.1]propellane (29) as an intermediate, which then reacts with the reagent used to give the observed products.[54] When the dehalogenation was carried out in the gas phase in an argon stream with potassium atoms as the reducing agent, followed by trapping the product as an argon matrix at 20 K, 29 was formed and could be identified via its infrared spectrum. When the matrix was warmed to 50 K, where it softens, the infrared spectrum disappeared, apparently via polymerization.[54] Ab initio calculations suggested a strain energy of 106 kcal/mol[6] and a central bond dissociation energy of only 30 kcal/mol.[3] Thus, the ready polymerization of 29 is not unexpected.



29

A bridged [2.1.1]propellane (30) was formed as an intermediate in a dehalogenation reaction:[55]

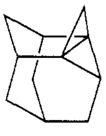


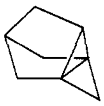
31 30 32

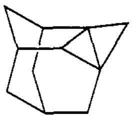
The reaction of 31 with butyllithium gave the metal–halogen exchange, but the lithium compound thus formed lost lithium chloride only slowly. The reaction in ether gave 32 as the major product, which is probably formed from 30. Other evidence for 30 as an intermediate was obtained.

The larger [*m*.1.1]propellanes are, as expected, less reactive than [2.1.1]propellane. [3.1.1]Propellane was prepared by a dehalogenation reaction and was found to be stable in solution at room temperature.[56] It was, however, more reactive than bicyclobutane. [4.1.1]-Propellane also has been prepared and can be isolated.[57] In pure form it readily polymerizes unless a free radical inhibitor is added.

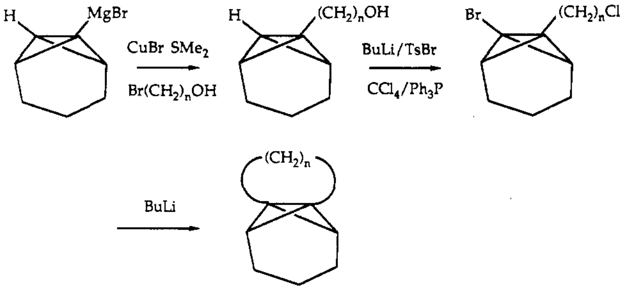
A number of bridged [*m*.1.1]propellanes have been prepared. Majerski et al. have obtained the [3.1.1]-propellane derivatives **33** and **34** via intramolecular carbene additions to double bonds.[58] A [4.1.1]propellane containing a *trans*-bicyclo[4.1.0]heptane unit (**35**) also has been prepared in this fashion.[59] They undergo facile reactions with electrophiles and free radicals, as well as a silver-catalyzed rearrangement to give a dimer similar to that found in the reaction with **1**.[60] It was possible to detect via ESR the radical formed by the addition of the trichloromethyl radical to **33**.[60]

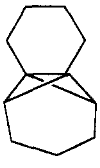

33

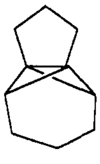

34

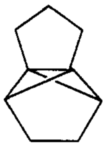

35

Two different approaches have been used by Szeimies et al. One was similar to that described above for bridged [1.1.1]propellanes. The cuprate derived from a bridged bicyclobutane such as **22** was first coupled with a bromo alcohol.[55] The product was converted to the dihalide and closed using butyllithium. Compounds prepared in this fashion include **36**–**38**. Whereas **36** can be stored in a refrigerator, **37** was isomerized to a diene in a few hours at 0 °C.

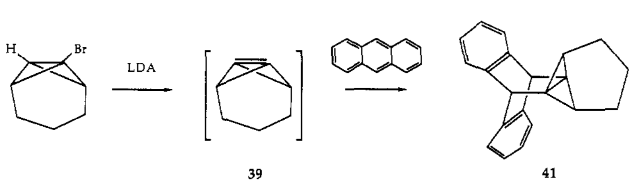


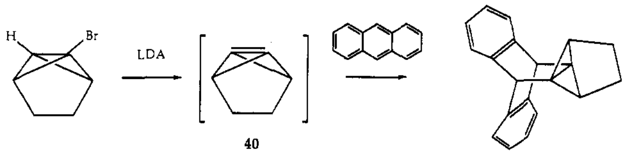

36


37


38

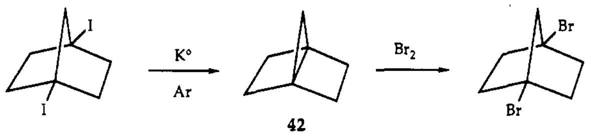
The second approach made use of the highly strained bicyclo[1.1.0]but-1(3)-ene derivatives **39** and **40**, which were formed as intermediates and were trapped by dienophiles as Diels–Alder adducts, giving compounds such as **41**.[61] Besides anthracene, other dienes that were used include 9-substituted anthracenes, furan, 2-methyl- and 2,5-dimethylfuran, diphenylisobenzofuran, and several isoindole derivatives. The structures of a number of these compounds have been determined by X-ray crystallography, and the central C–C bond lengths were in the range 1.54–1.57 Å.[13,62] Their reactions also have been studied in some detail.[63]





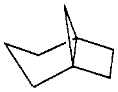
### 5. [*m*.2.1]Propellanes

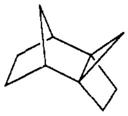
[2.2.1]Propellane (**42**) has received considerable study. The reaction of 1,4-dihalonorbornanes with lithium, alkyllithiums, and electrons (electrolysis) all give products that are best interpreted as being formed from **42**.[64] The available information suggests that it is very reactive toward electrophiles, nucleophiles, free radicals, and most other types of reagents. The successful preparation involved dehalogenation of 1,4-diiodonorbornane with potassium atoms in the gas phase, followed by capturing the product as an argon matrix at 20 K.[65] Evidence for the structure induced the infrared spectrum (propellanes have a characteristic intense C–C deformation mode around 600 cm$^{-1}$)[66] and its reaction with bromine to form 1,4-dibromonorbornane. Calculations suggest that the strength of the C$_1$–C$_4$ bond is minimal,[3,14] and it is observed that when the argon matrix is warmed to the softening point (50 K) the infrared spectrum of **42** disappears, presumably as a result of polymerization.[65] The estimated $\Delta H_f$ = 87 kcal/mol, corresponding to a strain energy of 109 kcal/mol.[6]

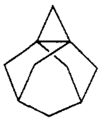


[3.2.1]Propellane (**43**) was the first of the small-ring propellanes to be prepared[67] and led to a general consideration of distortions at carbon. It is thermally quite stable but reacts readily with oxygen and undergoes free radical addition reactions;[67] it also reacts with electron-deficient alkenes and alkynes.[49] The enthalpy of formation may be estimated from its enthalpy of acetolysis[68] and from the enthalpy of formation of the 7-oxa derivative[69] and is $\Delta H_f$ = 39 kcal/mol (strain energy = 67 kcal/mol).[6]

A [3.2.1]propellane with an additional bridge (**44**) was prepared by Aue and Reynolds[49] and proved to be more reactive than **42**. Dehydroadamantane (**45**) is a [3.3.1]propellane,[70] but its properties are very similar to those of **42**, presumably because of the extra strain introduced by the added bridge. [4.2.1]Propellane was prepared by Warner and LaRose[71] and was found to have properties very similar to those of bicyclo[2.1.0]-pentane.


43

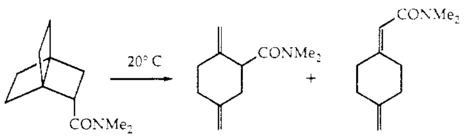

44


45

## 6. [m.2.2]Propellanes

[2.2.2]Propellane (**46**) is one of the most interesting of the small-ring propellanes. The first and only synthesis of a derivative of **46** was reported by Eaton and Temme in 1973 via ring contraction of a [3.2.2]propellanone.[72] The resulting amide (**47**) underwent a


46

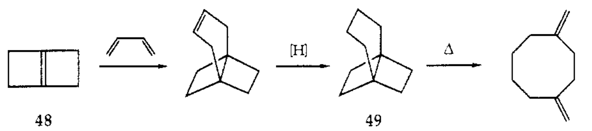


47

thermal cycloreversion with a half-life of only 1 h at 20 °C. The facile cleavage of **46** was in fact predicted by Stohrer and Hoffmann prior to its formation.[12] A bridged [2.2.2]propellane has been proposed as an intermediate in the dimerization of bicyclo[2.2.0]hex-1-(4)-ene and leads to the formation of a diene corresponding to those from **47**.[73]

[2.2.2]Propellane has received considerable theoretical study. The ab initio calculations of Newton and Schulman[74] confirmed that there were two diyls, one with a symmetric HOMO that is stabilized by a through-space interaction, and another with an antisymmetric HOMO that is stabilized by through-bond interactions. The most detailed study of **46** was reported by Feller and Davidson.[23] At the Hartree–Fock level, and using the 6-31G* basis set, two minima again were found, with central bond lengths of 1.6 and 2.5 Å and with comparable energies. There was a significant energy barrier separating them. Correction for electron correlation proved difficult because of the size of the molecule, and only a partial correction was possible. They now found that the barrier between the two forms was essentially zero. They concluded that the calculations "also raise the possibility that [2.2.2]propellane, as an isolated unsubstituted gas-phase molecule, may not exist". It is unfortunate that it has not as yet been possible to obtain the unsubstituted molecule so that its activation energy for thermolysis could be determined.

Some [*m*.2.2]propellane derivatives have been prepared via Diels–Alder reactions of bicyclo[2.2.0]hex-1-(4)-ene (**48**).[75] [4.2.2]Propellane (**49**) prepared in this fashion has a lower thermal reactivity than bicyclo-[2.2.0]hexane,[76] whereas **47** has a much higher reactivity. The low reactivity of **49** was attributed to the bridge, which prevents the bicyclo[2.2.0]hexane ring from opening in the normal fashion via a chair cyclohexane-1,4-diyl.[77] The high reactivity of **47** is reasonably attributed to its high strain energy, making the activation energy for going to a stretched 1,4-diyl relatively low. The estimated $\Delta H_f$ = 69 kcal/mol, leading to a strain energy of 97 kcal/mol, most of which would be relieved on central bond cleavage.[6]



48 49

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