

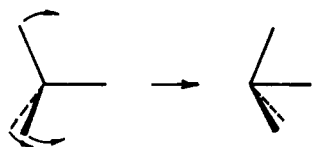
Inverted Geometries at Carbon

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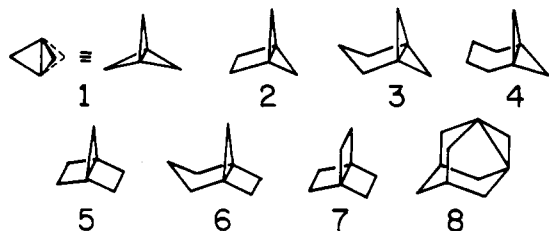
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One of the main structural elements in organic chemistry is the tetrahedral geometry of a four-coordinate carbon. Distortions from a perfect tetrahedron are common, but they are generally fairly small. It is, however, possible to "invert" the normal geometry via a C_{3v} or "umbrella" motion leading to a set of compounds having all of the groups attached to some carbon lying on one side of a plane.^{1,2}



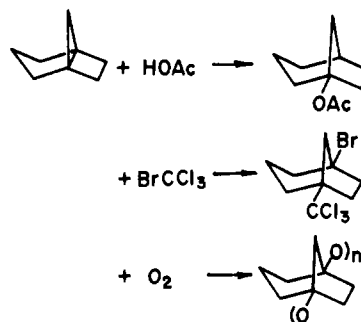
A number of compounds that are constrained to have this type of structure have now been prepared. The methods of preparation and their reactions and properties will be described below.³ It should be noted that inverted geometries may in some cases be found in the absence of structural constraint. Bicyclo[1.1.0]butane⁴ and its derivatives⁵ are notable examples, and the relationship between the geometry at the bridgehead and the flap angle has been examined in some detail by Gassman et al.⁵ Although there are similarities between bicyclobutane and many of the compounds discussed herein, its chemistry is outside the scope of this review.

The ultimate member of this series of compounds is [1.1.1]propellane (1).^{6,7} Intuitively, the geometry appears quite unreasonable, and it has been predicted to be incapable of existence.^{8,9} Less extreme geometries would be found with [2.1.1]propellane (2),¹⁰ [3.1.1]propellane (3),¹¹ [4.1.1]propellane (4),¹² [2.2.1]propellane (5),¹³ [3.2.1]propellane (6),¹⁴ and 1,3-dehydroadamantane (8).¹⁵ The criterion is almost met by the very interesting compound [2.2.2]propellane (7).¹⁶ All of these compounds have by now been prepared, either as the parent hydrocarbons or as derivatives!



Kenneth B. Wiberg received his B.S. from the Massachusetts Institute of Technology and Ph.D. from Columbia University. He joined the chemistry faculty at the University of Washington in 1950, was a visiting professor at Harvard, and moved to Yale University in 1962. He has held Sloan and Guggenheim fellowships, is a member of the National Academy of Sciences and the American Academy of Arts and Sciences, and received the J. F. Norris award in physical organic chemistry. His current research interests include small ring chemistry, thermochemistry, spectroscopy, and the application of ab initio MO theory to the study of organic chemical systems.

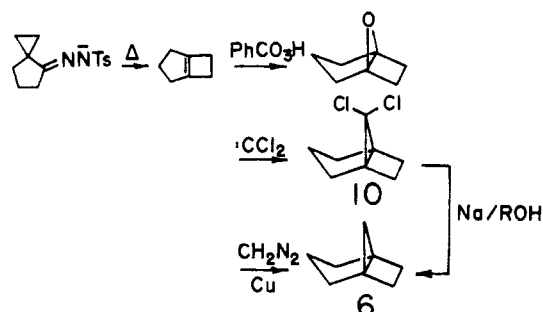
Scheme I



Preparative Methods

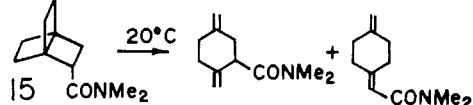
The first of these compounds to be prepared is 6 that is readily obtained from bicyclo[3.2.0]hex-1(5)-ene¹⁷ via cycloaddition reactions.^{1,14} The structure of the di-

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- (4) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969) (bridgehead C-H bond 11.5° below the plane formed from carbons 1, 2, and 4).
- (5) (a) P. L. Johnson and J. P. Schaefer, *J. Org. Chem.*, **37**, 2762 (1972); (b) P. G. Gassman and M. J. Mullins, *Tetrahedron Lett.*, 4457 (1979); (c) P. G. Gassman, M. L. Greenlee, D. A. Dixon, S. Richtsmeier, and J. Z. Gougoutas, *J. Am. Chem. Soc.*, **105**, 5865 (1983).
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- (12) (a) D. P. G. Hamon and V. C. Trenerry, *J. Am. Chem. Soc.*, **103**, 4962 (1981); (b) U. Szeimies-Seebach, J. Harnish, G. Szeimies, M. V. Meerssche, G. Germain, and J. P. Declercq, *Angew. Chem., Int. Ed. Engl.*, **17**, 848 (1978); (c) U. Szeimies-Seebach, A. Schoeffer, R. Roemer, and G. Szeimies, *Chem. Ber.*, **114**, 1767 (1981); (d) U. Szeimies-Seebach and G. Szeimies, *J. Am. Chem. Soc.*, **104**, 2056 (1982); (e) J.-P. Declercq, G. Germain, and M. Van Meerssche, *Acta Crystallogr., Sect. B* **B34**, 3472 (1978).
- (13) F. H. Walker, K. B. Wiberg, and J. Michl, *J. Am. Chem. Soc.*, **104**, 2056 (1982).
- (14) (a) K. B. Wiberg and G. Burgmaier, *Tetrahedron Lett.*, 317 (1969); *J. Am. Chem. Soc.*, **94**, 7396 (1972); (b) P. G. Gassman, A. Topp, and J. W. Keller, *ibid.*, 1089 (1969); (c) D. H. Aue and R. N. Reynolds, *J. Org. Chem.*, **39**, 2315 (1974).
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- (17) W. Kirmse and K. H. Pook, *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966).



chloride **10** was determined by X-ray crystallography,¹⁸ and it was found that a plane drawn through the three carbons attached to a bridgehead carbon would intersect the central bond 0.1 Å in from the bridgehead carbon. Thus it does have an "inverted" geometry. The hydrocarbon **6** was remarkable in that it reacted very quickly with acetic acid to cleave the central carbon-carbon bond and it reacted quickly with free radicals and with oxygen (Scheme I).^{14a} On the other hand, it was quite resistant to thermolysis and underwent cleavage to 1,3-dimethylenecyclohexane only at 320 °C.

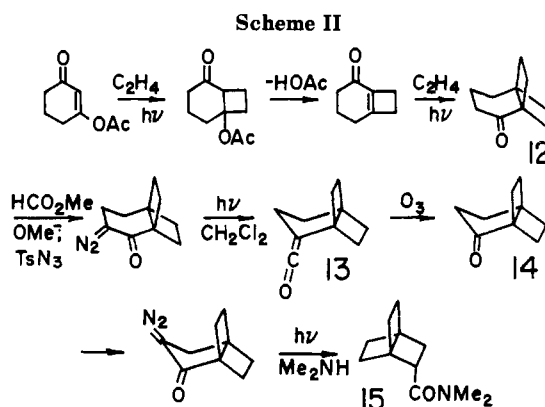
The next compound to be prepared was a derivative of [2.2.2]propellane via the elegant procedure described by Eaton and Temme (Scheme II).¹⁶ Photochemical cycloadditions led to the [4.2.2]propellan-2-one (**12**) that was converted to its diazo ketone and photolyzed to give the ring contracted ketene (**13**). Ozonization converted the ketene to a ketone (**14**). A second ring contraction in the presence of dimethylamine gave *N,N*-dimethyl-[2.2.2]propellane-2-carboxamide (**15**). Unlike [3.2.1]-propellane, **15** was relatively unreactive toward weak electrophiles—but it underwent thermolysis at room temperature.



The remarkable difference in reactivity between the isomeric ring systems in **6** and **15**, i.e., **6** being very reactive toward electrophiles and free radicals but unreactive toward thermolysis whereas **15** is relatively unreactive toward electrophiles and free radicals but very reactive toward thermolysis, has made the compounds of considerable interest to chemists. These properties, along with the unusual structural features, have led to a number of investigations leading to new members of the series.

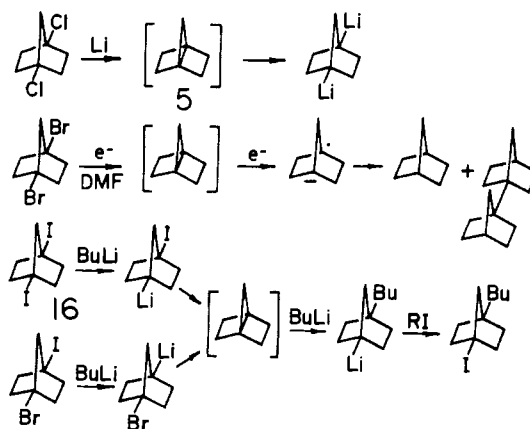
The [2.2.1]propellane has been the subject of several investigations. In an attempt to convert 1,4-dichloronorbornane to the 1,4-dicarboxylic acid, Wilcox and Leung¹⁹ treated the dichloride with lithium and carbonated the product. The diacid was formed, but in no case was 1-chloronorbornane-4-carboxylic acid found. The simplest explanation would propose **5** as an intermediate that could react with lithium to form the 1,4-dilithio intermediate.

We have studied the electrolytic reduction of 1,4-dibromonorbornane.²⁰ Whereas this reaction is suc-



cessful in preparing **6** from 1,5-dibromobicyclo[3.2.1]octane, only norbornane and binorbornyl were found. Both could be formed by reduction of **5** if it were an intermediate. Subsequently, Carroll and Peters²¹ showed that 1-bromonorbornane was not an intermediate (i.e., the halogens were not removed one at a time) and that the reaction involved a three-electron reduction. This strongly suggests that **5** was an intermediate.

Reduction of 1,4-diiodonorbornane with butyllithium would be expected to be successful in forming **5** since 1-iodonorbornane reacts quantitatively to give 1-lithionorbornane.²² In this case, the diiodo compound reacted to replace one iodine by butyl, and 1-bromo-4-iodonorbornane gave the same product.²³ Again, **5** was probably an intermediate.



These observations suggest that **5** will be reactive toward nucleophiles and the addition of electrons. It also would be expected to be even more reactive than **6** toward electrophiles and free radicals. How can **5** be prepared in the absence of these reagents? One possibility was to carry out the dehalogenation of **16** in the gas phase using a reducing agent such as potassium atoms. The iodines of an alkyl halide have a high enough electron affinity to permit an electron transfer from potassium atoms. Once formed, **5** should not be able to accept electrons from potassium in the gas phase. This reaction, which has been used to prepare some reactive alkenes,²⁴ was found to be successful.¹³

(21) W. F. Carrol, Jr., and D. G. Peters, *Tetrahedron Lett.*, 3543 (1978). W. F. Carrol, Jr., and D. G. Peters, *J. Am. Chem. Soc.*, **102**, 4127 (1980).

(22) P. T. Lansbury and J. D. Sidler, *Tetrahedron Lett.*, 691 (1965).

(23) K. B. Wiberg, W. E. Pratt, and W. F. Bailey, *J. Am. Chem. Soc.*, **99**, 2287 (1977).

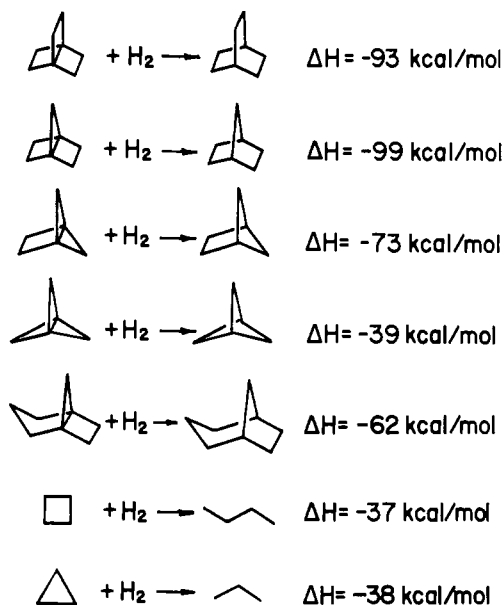
(24) K. L. Taeng and J. Michl, *J. Am. Chem. Soc.*, **99**, 4840. R. T. Conlin, R. D. Miller, and J. Michl, *ibid.*, **101**, 7637 (1979).

(18) K. B. Wiberg, G. J. Burgmaier, K. Shen, J. LaPlaca, W. C. Hamilton, and M. D. Newton, *J. Am. Chem. Soc.*, **94**, 7402 (1972).

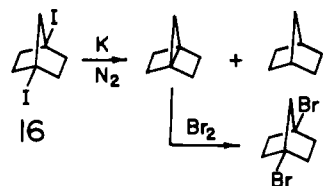
(19) C. F. Wilcox, Jr., and C. Leung, *J. Org. Chem.*, **33**, 877 (1968).

(20) (a) K. B. Wiberg, W. F. Bailey, and M. E. Jason, *J. Org. Chem.*, **41**, 2711 (1976); (b) M. R. Rifi, *Collect. Czech. Chem. Commun.*, **36**, 932 (1971).

Scheme III



The compound was trapped in a nitrogen matrix at ~ 30 K. The infrared spectrum showed the presence of norbornane along with a new compound having a cyclopropyl C-H stretching band at 3065 cm^{-1} and a very intense band at 575 cm^{-1} that is characteristic of propellanes and related compounds. When bromine vapor was sprayed on the matrix as it was formed, 1,4-dibromonorbornane was found as the product. These data indicate that [2.2.1]propellane was formed.

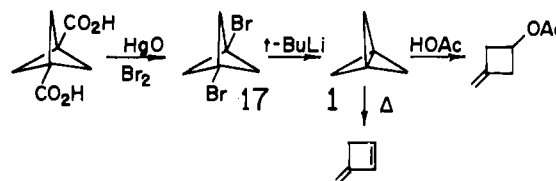


The success of this preparation led us to ask if it might be possible to prepare 1 and 2 by the same method. In recent years it has become practical to calculate the energies and geometries of compounds such as these with reasonable accuracy via ab initio MO methods.²⁵ A simple model for the dehalogenation reactions is the reverse of hydrogenolysis of the central C-C bond. Thus, the energies of hydrogenolysis were calculated by using an extended basis set that included d functions at carbon.²⁶ This was found to be necessary with highly strained compounds (Scheme III).

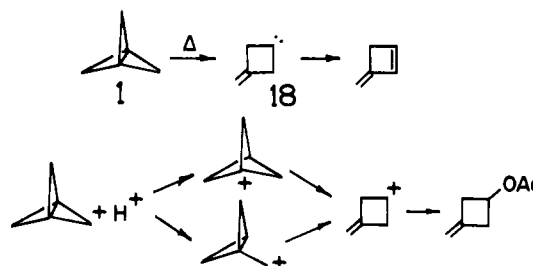
The remarkable result was that the energy of hydrogenolysis of 1 was virtually the same as that for cyclopropane or cyclobutane. Thus, 1 should easily be prepared from the corresponding dihalide. Further, the energies of possible intermediates for the reaction of 1 with free radicals or on thermolysis were calculated to be large, suggesting that 1 should be a relatively stable molecule.

Bicyclo[1.1.1]pentane-1,3-dicarboxylic acid²⁷ was converted to the dibromide 17, and this was treated with *tert*-butyllithium to give 1.⁶ In accord with the

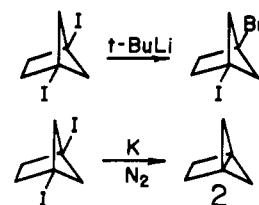
calculations, 1 was stable at room temperature and only underwent thermolysis above $100\text{ }^\circ\text{C}$ to give 3-methylenecyclobutene. Reaction of 1 with acetic acid gave 3-methylenecyclobutyl acetate.⁶



The thermolysis probably involves the reverse of a carbene insertion into a double bond; the calculated difference in energy between the propellane and the carbene 18 is close to the activation energy for the thermolysis ($\sim 30\text{ kcal/mol}$). It will be interesting to learn whether or not 18, formed via an independent route, will lead to some 1 in competition with hydrogen migration. The reaction with acetic acid could involve attack by proton at a bridgehead carbon cleaving either of two carbon-carbon bonds. Both cations have been studied and are known to give 3-methylenecyclobutyl products.²⁸



The [2.1.1]propellane(2) could be prepared in the same manner as used for 5. The reaction of 1,4-diiodobicyclo[2.1.1]hexane with *tert*-butyllithium gave mainly 1-*tert*-butyl-4-iodobicyclo[2.1.1]hexane, presumably via the propellane as an intermediate. When the diiodide was treated with potassium in the gas phase and the product trapped in a nitrogen matrix, infrared bands expected for 2 were found.¹⁰ The de-



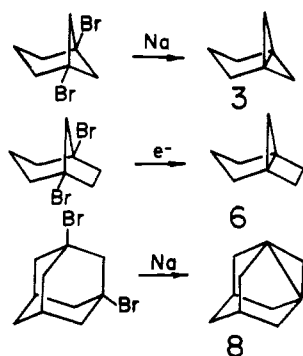
halogenation reactions appear to be generally useful for the preparation of propellanes containing a cyclopropane ring. [3.1.1]Propellane (3),^{11a} [3.2.1]propellane,²⁰ and 1,3-dehydroadamantane¹⁵ were prepared in solution by this method. Butyllithium is frequently a useful alternate reducing agent for the formation of this type of propellane.²³

In some cases, it has proven possible to obtain small ring propellanes via a carbene insertion into a double bond (Scheme IV). The Diels-Alder reaction is another generally useful reaction for the preparation of small ring propellanes. Some examples of this method are as shown in Scheme V.²⁹

(25) J. A. Pople, *Mod. Theor. Chem.*, 4, 1 (1977).
 (26) K. B. Wiberg, *J. Am. Chem. Soc.*, 105, 1227 (1983).
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Properties

The properties of interest include the structures, the energies, and the spectra. In a few cases, structural data are available from X-ray crystallography. The structures are summarized in Figure 1. Despite the considerable variation in ring sizes, the central bond length is remarkably constant in the range 1.55–1.58 Å. The most interesting observation derived from the structural studies is the low deformation density in the central bond of the [3.1.1]propellane derivative 19.³⁰ The deformation density is the difference between the observed electron density distribution and that expected for spherically symmetrical atoms at the corresponding positions. Thus, it is the electron density associated with bond formation.³¹ The low deformation density also has been found in theoretical calculations for the [*n*.1.1]propellanes.^{7,26} The bonding in [1.1.1]propellane has been discussed.³²

Very little experimental data are available concerning the energies of the propellanes. The reactions of 6 and 8 with acetic acid have been studied calorimetrically (Scheme VI).³³ From these data, one may deduce that the strain energies of 6 and 8 are 67 and 64 kcal/mol, respectively. This is in good accord with the estimate of 66 kcal/mol derived from the enthalpy of combustion of 7-oxa[3.2.1]propellane.³⁴

In view of the relatively small amount of experimental data, it is helpful to examine the results of theoretical calculations dealing with these compounds. It was found that consistent relative energies could be obtained in ab initio calculations only when d orbitals were included at carbon.²⁶ Apparently, the inverted tetrahedral geometry cannot be adequately described with just s and p orbitals, and d orbitals must be added to give greater flexibility to the basis set. The calculated geometries of several of the propellanes are shown in Figure 2. The C–C and C–H bond lengths derived from these calculations are generally 0.01 Å too short, whereas the calculated bond angles are normally very close to the experimental values.³⁵ It can be seen that

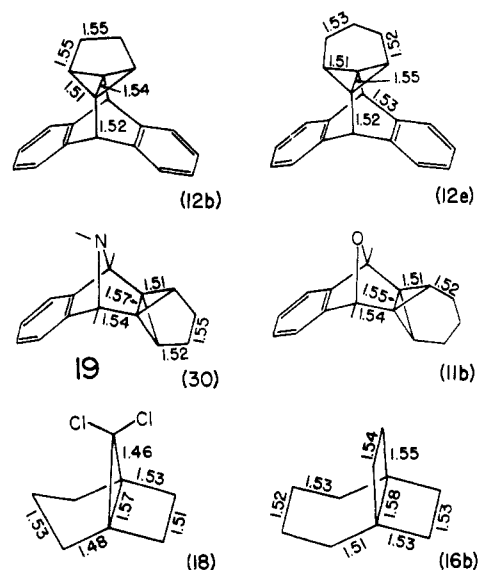
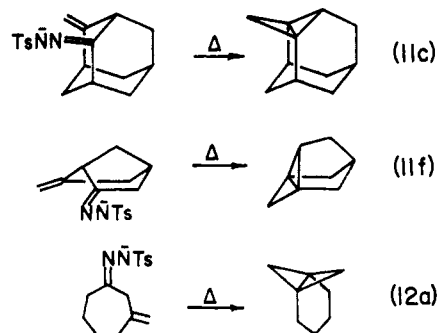
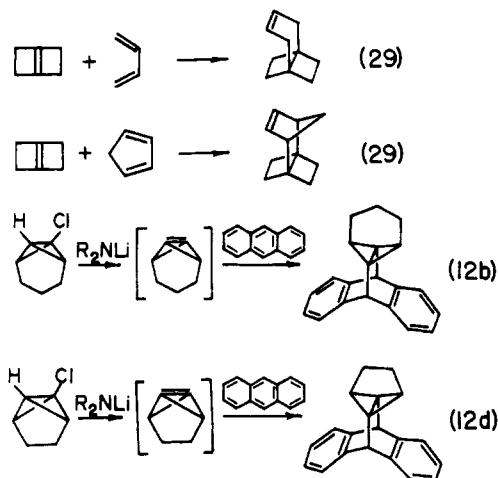


Figure 1. Structures of propellanes as determined by X-ray crystallography.

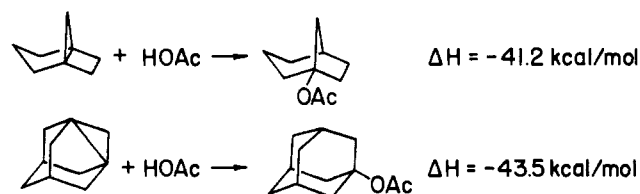
Scheme IV



Scheme V



Scheme VI



the structures of the compounds are quite normal, with calculated C–C bond lengths on the order of 1.50–1.59 Å.

(29) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Am. Chem. Soc.*, **93**, 246 (1971); K. B. Wiberg and M. E. Jason, *ibid.*, **98**, 3393 (1976).

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N. D. Epiotis, "Unified Valence Bond Theory of Electronic Structure. Applications", Springer Verlag, New York and Berlin, 1983, Vol. 34, p 379.

(33) K. B. Wiberg, H. A. Connon, and W. W. Pratt, *J. Am. Chem. Soc.*, **101**, 6970 (1979).

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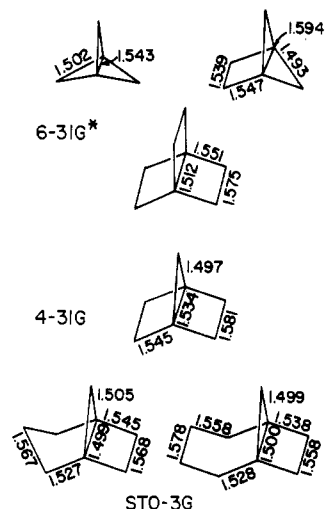


Figure 2. Calculated structures of propellanes. The upper three were obtained by using the 6-31G* basis set, the middle was obtained by using the 4-31G basis set, and the lower two were obtained by using the STO-3G basis set.

Table I
Enthalpies of Formation of Propellanes

compd	ΔH_f	SE	source
[1.1.1]propellane (1)	89	102	a
[2.1.1]propellane (2)	86	104	a
[2.2.1]propellane (5)	79	102	a
[2.2.2]propellane (7)	65	93	a
[3.2.1]propellane (6)	39	67	b
[3.2.2]propellane	32	65	c
[4.2.2]propellane	17	55	c

^a Reference 34. ^b Reference 32. ^c Calculated using the MM2³⁸ force field.

It is unfortunately not possible to make a detailed comparison with the experimental structures. The only common structure is [3.2.1]propellane, and here the experimental data refer to the dichloro derivative. The effect of chlorine substitution on the structure is not known. Similarly, the geometry optimization for this large a compound could only be carried out by using the STO-3G basis set, and it remains to be determined whether or not a larger basis set will result in a significant change in geometry. More experimental data and theoretical calculations are needed.

It has been found that ab initio energies using the 6-31G* basis set may be converted to enthalpies of formation with an average uncertainty of ± 2 kcal/mol via the use of a set of group equivalents.³⁶ In this way, the calculated energies lead to the enthalpies of formation and strain energies listed in Table I. In the case of [3.2.1]propellane, the number given in the table is derived from experimental measurements. It can be seen that the strain energies of 1, 2, and 5 are remarkably constant. It decreases 10 kcal/mol in going to 7 and another 25 kcal/mol on going to 6. We will see later that the high strain energies of some of these compounds are important in determining their reactivity.

When dealing with compounds that have less severe distortion, it is frequently possible to make use of molecular mechanics. This is far less expensive than molecular orbital calculations and again gives both structures and energies. The calculation for bicyclo[2.2.0]hexane gives an energy that agrees well with the ex-

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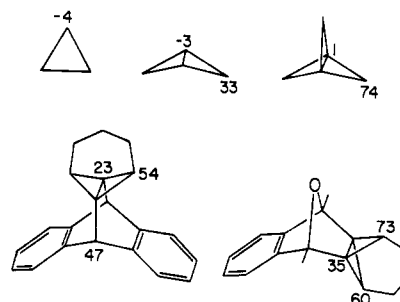
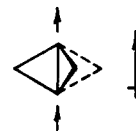


Figure 3. ¹³C NMR chemical shifts for compounds having a bicyclobutane unit.

perimental value derived from the enthalpy of hydrogenation and the enthalpy of formation of cyclohexane.³⁷ The estimated enthalpies of formation of [3.2.2]- and [4.2.2]propellanes were derived from molecular mechanics calculations using Allinger's MM2 parameter set.³⁸

The infrared spectra of propellanes 2 and 5 have been of special interest to us because they provide one of the ways of characterizing the compounds as matrix-isolated species. Both have a characteristic cyclopropane C-H stretching band at about 3300 cm^{-1} , and of more importance, they have a very strong band at ~ 550 cm^{-1} . The latter appears to be characteristic of these propellanes and related compounds such as 1, 6, and bicyclo[1.1.0]butane.³⁹ Normal-coordinate analyses⁴⁰ as well as theoretical calculations^{41,42} have shown that the mode is an antisymmetric C-C stretch that leads to a motion of the bridgehead carbons with respect to the rest of the carbon framework:



This vibrational mode leads to the formation of a large dipole in the direction shown and results in a high intensity for the band.

The ¹H NMR spectrum of 1 has a singlet at δ 2.06, and the ¹³C spectrum has a band at δ 74 for the CH₂ group ($J_{13\text{C-H}} = 165$ Hz) and a band at δ 1 for the bridgehead carbons.⁶ The ¹³C NMR spectra of some propellanes having a bicyclo[1.1.0]butane unit are compared with those of cyclopropane and bicyclobutane in Figure 3. It can be seen that structural changes have an unusually large effect on the chemical shifts.

Reactivity

There is a remarkable range of thermal stabilities observed with compounds 1 through 8. [2.1.1]Propellane (2) and [2.2.1]propellane (5) can be observed only in a solid matrix at low temperature, and when the matrix is warmed to the softening point, the compounds

(37) W. R. Roth, F.-G. Klärner, and H.-W. Lennartz, *Chem. Ber.*, **113**, 1818 (1980).

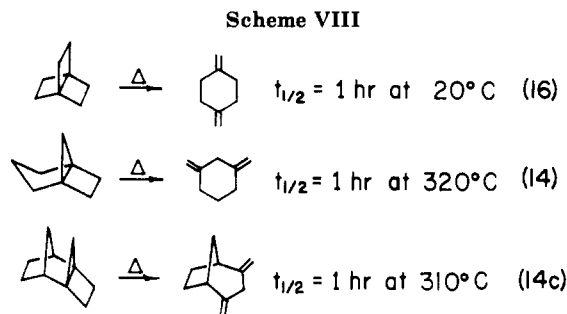
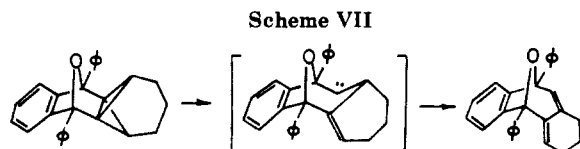
(38) U. Burkert and N. L. Allinger, *ACS Monogr.*, No. 177 (1982).

(39) The corresponding frequencies for 1, 6, and bicyclo[1.1.0]butane are 603, 574, and 735 cm^{-1} , respectively.

(40) K. B. Wiberg and K. S. Peters, *Spectrochim. Acta, Part A*, **33A**, 261 (1977); K. B. Wiberg, D. Sturmer, T. P. Lewis, and I. W. Levin, *ibid.*, **31A**, 57 (1975).

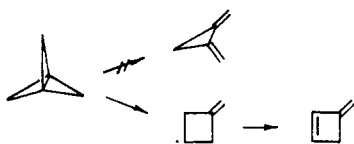
(41) J. Michl, G. J. Radziszewski, J. W. Downing, K. B. Wiberg, F. H. Walker, R. D. Miller, P. Kovacic, M. Jawdoskiuk, and V. Bonacic-Koutecky, *Pure Appl. Chem.*, **55**, 315 (1983).

(42) Unpublished ab initio calculations at Yale.



polymerize.^{10,13} This behavior is not surprising in view of their high strain energies, which leads to a highly exothermic addition of a free radical across the central bond. Despite the equally high strain energy of [1.1.1]propellane (1), it is resistant to polymerization because the radical formed by addition to the central bond is destabilized by both the geometry at the bridgehead and the strain inherent in the bicyclo-[1.1.1]pentane ring system. Polymerization also has been noted with [3.1.1]propellane, although the temperature at which the reaction occurs is much higher than for 6 or 8.¹¹

The thermolysis of the propellanes has received considerable study. In the case of the [n.1.1]propellanes, two mechanistically different paths are available. In the first, bond cleavage might occur with retention of the central bond as is found with bicyclo[1.1.0]butane.⁴³ With [1.1.1]propellane as an example, the product would be 1,2-dimethylenecyclopropane. In the second, a retro-carbene addition occurs, which would be followed by hydrogen migration to again yield a diene. In this case, the product would be 3-methylenecyclobutene. The latter course was observed experimentally.⁶

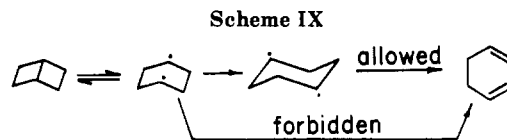


The [3.1.1]- and [4.1.1]propellanes obtained by Sziemias et al.^{11,12} reacted in the same fashion (Scheme VII).

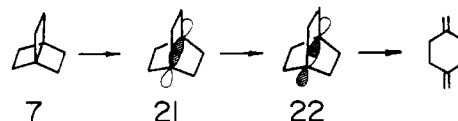
Propellanes having a cyclobutane ring react via direct cleavage of the ring to form a diene (Scheme VIII). In the case of cyclobutane, this process is orbital symmetry forbidden as a concerted process, and accordingly, it has a high activation energy. Two different mechanisms have been proposed for the cleavage of bridge cyclobutanes. In the case of [2.2.2]propellane, the calculations of Strohrer and Hoffmann⁴⁴ suggest that the initially formed symmetric diradical 21 would be converted to the more stable antisymmetric diradical 22. The latter may undergo an orbital symmetry-allowed

(43) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(44) W. D. Strohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 779 (1972).



cleavage to 1,4-dimethylenecyclohexane (bond stretch isomerization). The lower energy of 22 depends on the flexibility of the bicyclo[2.2.2]octane ring system that permits a large enough bridgehead-bridgehead distance to bring the symmetric (through space bonding) and antisymmetric (through space antibonding) diradicals close in energy, coupled with a the stabilization of 22 by a through-bond interaction with the σ^* orbitals of the ethano bridges. A more detailed calculation by Newton and Schulman⁴⁵ gave corresponding results for the difference in energy between 21 and 22. This mechanism could account for the greatly increased activation energy for [3.2.1]propellane in that the diradical will have a relatively short bridgehead-bridgehead distance because of the constraint introduced by the one carbon bridge. Thus, in this case the symmetric diradical will always be at lower energy than the antisymmetric, and the reaction will proceed via an orbital symmetry-forbidden cleavage of the former.



A rather different mechanism has been proposed for the thermolysis of bicyclo[2.2.0]hexane, which is structurally similar, but missing one two-carbon bridge. Here, Goldstein⁴⁶ has shown that the ring inversion process proceeds more rapidly than cleavage, and several investigators have shown that the stereochemistry of the product corresponds to an orbital symmetry-allowed cleavage of the chair cyclohexane-1,4-diyl.⁴⁷ The reaction probably proceeds as shown in Scheme IX.

In order to see how bridging affects the cleavage of the bicyclo[2.2.0]hexane structural unit, we have examined the thermolysis of some [3.2.2]- and [4.2.2]propellanes.⁴⁸ In these cases, the activation energy increased from the 36 kcal/mol observed with 22⁴⁶ to 41-46 kcal/mol. The increase in activation energy is easily explained in terms of the above mechanism in that a bridge will prevent the conformational change of the boat diradical to the chair. The reaction must then proceed directly from the boat diyl by a "forbidden" pathway with a higher activation energy.

If bridging normally increases the activation energy, what can be said about [2.2.2]propellane? Both [3.2.2]- and [4.2.2]propellanes have the flexibility required to provide a relatively large bridgehead-bridgehead distance in the diradical, and both have two σ^* orbitals that may help to stabilize the antisymmetric diyl. Thus, there should not be a marked mechanistic difference between the reactions of the three propellanes. Nev-

(45) M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.*, **94**, 4391 (1972).

(46) M. J. Goldstein and M. S. Benzon, *J. Am. Chem. Soc.*, **94**, 7147 (1972).

(47) L. A. Paquette and J. A. Schwartz, *J. Am. Chem. Soc.*, **92**, 3215 (1970); A. Sinnema, F. van Rantwijk, A. J. De Koning, A. M. van Wijk, and H. van Bekum, *Tetrahedron*, **32**, 364 (1973); R. Wehrli, D. Bellus, H.-J. Hansen, and H. Schmid, *Chimia*, **30**, 416 (1976).

(48) K. B. Wiberg and M. Maturro, *Tetrahedron Lett.*, 3481 (1981).

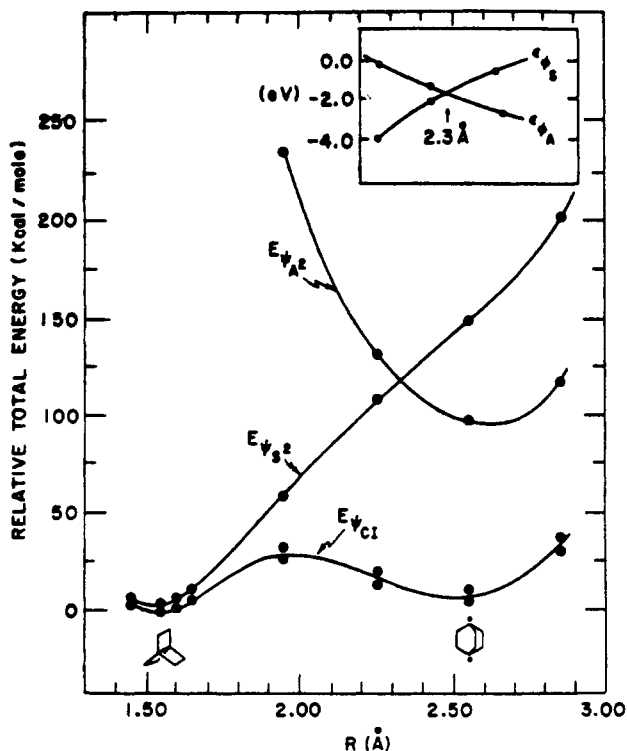
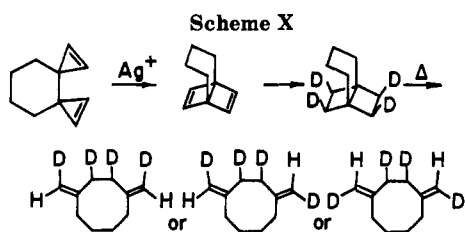


Figure 4. Total SCF energies for the symmetric ($E_{\psi_{s^2}}$) and antisymmetric ($E_{\psi_{a^2}}$) diyls and CI energies as a function of the central CC bond length from ref 43.



ertheless, [2.2.2]propellane has a much lower activation energy than either of these compounds or bicyclo[2.2.0]hexane.

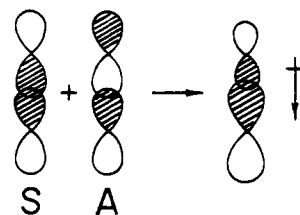
The high reactivity of [2.2.2]propellane can be accounted for without a change in mechanism since its strain energy is about 30 kcal/mol greater than that for the other propellanes. If much of this increased energy can be used to reduce the activation energy, a low value would be expected.

An examination of the energy diagram for [2.2.2]propellane given by Newton and Schulman is instructive in this context (Figure 4). The calculation predicted the activation energy quite well (calcd, 27 kcal/mol; obsd, 22 kcal/mol).⁴⁵ It will be seen that the activated complex appears at a bridgehead-bridgehead separation of 1.9 Å whereas the symmetric-antisymmetric crossing appears at 2.3 Å. Thus, the calculated activation energy is concerned with the symmetric diyl! The Stohrer-Hoffman mechanism may become important in the product-determining step and should define the stereochemistry of the reaction. This cannot easily be studied with **5** because of its high symmetry but could be more easily examined with [4.2.2]propellane. Here, a simple path to a suitable compound is available (Scheme X).⁴⁹

(49) I. J. Landheer, W. H. deWolf, and F. Bickelhaupt, *Tetrahedron Lett.*, 2183 (1974).

Another important reaction of the small ring propellanes is their C-C bond cleavage with electrophiles. We have found that [3.2.1]propellane (**6**) reacts with acetic acid essentially instantaneously, cleaving the central bond.³⁸ On the other hand, [2.2.2]propellane (**7**) appears to have a relatively low reactivity toward weak electrophiles, although it does react readily with stronger electrophiles such as the halogens.¹⁶ The difference in reactivity appears to be directly related to the general observation that cyclopropanes are much more reactive toward electrophiles than are cyclobutanes. Thus, cyclopropane reacts with halogens whereas cyclobutane does not. Similarly, bicyclo[2.1.0]pentane reacts with acetic acid whereas bicyclo[2.2.0]hexane does not.⁵⁰ The reason for the difference in reactivity can be found in the difference between the energies and structures of protonated cyclopropanes and cyclobutanes.⁵⁰

There is a marked difference in reactivity between [3.2.1]- and [4.2.1]propellane with the former being 10^4 more reactive than the latter.⁵¹ The ionization potentials and electron density distributions of the two hydrocarbons are essentially the same and indicate no reasons for the difference in reactivity. The reactions probably involve the formation of a corner-protonated cyclopropane as an intermediate or activated complex. Thus, polarization of the central bond is an essential part of the reaction. Polarization involves the mixing of an unoccupied orbital that is antisymmetric with respect to the central bond with the highest occupied orbital that is symmetric. The energies of the latter are the same for the two compounds. However, the former do not correspond to the lowest unoccupied molecular orbitals, and their energies are quite different. This accounts for the difference in reactivity. These considerations should be important for any case of unsymmetrical electrophilic or nucleophilic attack on a molecule.



Unlike [3.2.1]propellane, which reacts readily with oxygen and free radicals, [2.2.2]propellane, which has more potential strain energy relief associated with cleaving the central bond, does not appear to react with these species. It may be possible that the factors responsible for the difference in reactivity toward electrophiles are also important in the reaction with free radicals.

Concluding Remarks

Small ring hydrocarbons have frequently been used in studies of chemical bonding, mechanisms of thermal rearrangements, mechanisms of carbon-carbon bond cleavage by electrophiles, stabilization of carbocations, and a variety of other problems of interest to chemists. Their utility depends on the changes in C-C bonds that result from bond angle deformation (i.e., rehybridization

(50) K. B. Wiberg, K. C. Bishop, III, and R. B. Davidson, *Tetrahedron Lett.*, 3169 (1973).

(51) K. B. Wiberg and S. Kass, to be submitted for publication.

and the formation of bent bonds) and the related increases in energy. The small ring propellanes carry bond angle deformation to an extreme and lead to new types of reactions that have not been observed with mono- or bicyclic small ring systems. The remarkable stability of [1.1.1]propellane again shows the importance of driving force for a particular reaction vs. the overall strain energy. Further studies of these com-

pounds should give chemists a much better understanding of the nature of carbon-carbon bonds.

I am indebted to my co-workers, whose names appear in the references, for their contributions to our studies of small ring chemistry. I should like to acknowledge the valuable collaboration with Prof. J. Michl in the preparation of some of the propellanes. The investigations were supported by grants from the National Science Foundation.

Stable Compounds with Double Bonding between the Heavier Main-Group Elements

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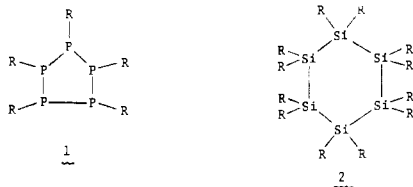
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With the advent of modern structural techniques, compounds that were thought to possess $P=P^1$ or $Si=Si^2$ bonds have been shown subsequently to be cyclic oligomers.³ As a consequence of these and allied observations, the consensus developed that compounds featuring (p-p) π -bonds between the heavier main-group elements would not be stable. Such a view is often referred to as "the double-bond rule". Significant progress in the area was not forthcoming until 1965, when Gusel'nikov et al.⁴ developed a methodology for the production of transient silaethenes. Since then, evidence for numerous other ephemeral species with implied double bonds between silicon and phosphorus atoms has been presented.⁵ However, the isolation and characterization of *stable* compounds of this genre is a much more recent accomplishment and represents the subject matter of this Account.

Thermodynamic and Kinetic Factors

The basic difficulty underlying the isolation of compounds with multiple bonding between heavier main-group elements is thermodynamic. Consider the following representative bond energy data (kcal/mol) for single and multiple bonds:⁶ N—N (39), N=N (100.1), N≡N (225.8), P—P (48), P=P (74), P≡P (117). Two trends are evident: (i) the relative increase in bond energy with bond order is much greater for the first-row element than for the heavier congener, and (ii) for the heavier main-group elements, it is more favorable to form two σ -bonds than one σ - and one π -bond. As a consequence, species of empirical composition RP or R_2Si usually exist as cyclic oligomers like 1 and 2 rather



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than as diphosphenes ($RP=PR$) or disilenes ($R_2Si=SiR_2$). One obvious way to thwart the oligomerization tendency of the doubly bonded compounds is by increasing the steric demands of the substituents, R. Although the stabilization of diphosphenes or disilenes by steric blockades might be thought of as primarily kinetic, it should be borne in mind that some of the stabilization is thermodynamic in origin since the steric interactions among the bulky groups are less in diphosphenes or disilenes than in the corresponding cyclic species. Another approach to double-bond formation is to take advantage of the enhanced stability of lower coordination numbers with increasing atomic number—the so-called "inert s-pair effect".

Group 4A Compounds. The group 4A alkyls, $[(Me_3Si)_2CH]_2E$, $E = Ge, Sn, \text{ and } Pb$, were prepared by Lappert and co-workers several years ago.⁷ All compounds are monomeric in the vapor phase and exhibit the anticipated V-shaped structures. However, in the solid state, the tin and germanium compounds are dimeric and feature bonding between the E atoms, viz., $[(Me_3Si)_2CH]_2EE[CH(SiMe_3)_2]_2$ ($E = Ge$ (3) and Sn (4)). As will be discussed in a subsequent section, questions have arisen regarding the exact nature of the central bond. Nevertheless, these compounds represent the first examples of stable compounds involving homonuclear double bonding between the heavier group 4A or 5A elements.

The first stable disilene, $(Mes)_2Si=Si(Mes)_2$ (5) ($Mes = 2,4,6-Me_3C_6H_2$), was prepared by West et al.⁸ via the

- (1) Köhler, H.; Michaelis, A. *Ber. Dtsch. Chem. Ges.* 1877, 10, 807.
- (2) Kipping, F. S. *Proc. Chem. Soc.* 1911, 27, 143.
- (3) For X-ray data, see e.g. (a) Daly, J. J. *J. Chem. Soc.* 1965, 4789.
- (b) Hedberg, K.; Hughes, E. W.; Waser, J. *Acta Crystallogr.* 1961, 14, 369.
- (4) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* 1975, 8, 18 and references therein.
- (5) For a review, see (e.g.) Gaspar, P. P. "Reactive Intermediates", Jones, M., Moss, R. S., Eds.; Wiley: New York, 1978; Vol. 1, Chapter 7.
- (6) Data from the following: (a) Cottrell, T. L. "The Strengths of Chemical Bonds", 2nd ed.; Butterworths: London, 1958. (b) Fehlner, T. P. *J. Am. Chem. Soc.* 1966, 88, 1819.
- (7) (a) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* 1976, 261. (b) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* 1976, 2268. (c) Fjeldberg, T.; Lappert, M. F.; Schilling, B. E. R.; Seip, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* 1982, 1407.