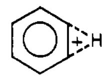
Table II. Activation Energies for Interstructural Conversions in the $C_6H_5^+$ System (kcal/mol)[a]

	1	2	3	5	6	10	11	12
1		62	62	69	40	69	65	78
2	47		13	54	25	54	50	63
3	46	12		53	24	53	49	62
5	32	32	32		32	23	32	41
6	1	1	1	29		25	25	38
10	14	14	14	5	14		14	23
11	3	3	3	7	3	7		16
12	10	10	10	10	10	10	10	

[a] The figures in the *i*th row show the activation energies for the structural conversion from the structure *i*, while those in the *j*th column express the conversion from the structure *j*. For example, the activation energy from 1 to 2 is read as 62 kcal/mol, whereas from 2 to 1 it is 47 kcal/mol.

in Figure 8 where the heats of formation are plotted against three different reaction coordinates; for **1** → **11** the reaction coordinate is the distance (R) between C_2 and C_6 in **1** for **12** → **5** and **5** → **10**, the reaction coordinate is the angle (θ) of C_1 in the molecular plane (see **11** and **5** in Figure 8). The highest potential energy appears to be **11** → **5**—314 kcal/mol; the activation energy is, therefore, 69 kcal/mol. It should be stressed that this value and the activation energy for **1** → **6** are far lower than the energy required for fragmentation, indicating that the carbon atoms in the phenyl cation can be randomized prior to fragmentation.

It has been reported that before the loss of C_2H_2 from the $C_6H_5^+$ ion, which is produced from iodobenzene by electron impact, the six carbon and hydrogen atoms are completely randomized.[30] The heat of formation of $C_6H_5^+$ from iodobenzene has been measured to be 299 kcal/mol.[31] This value is 54 kcal/mol higher than that of the ground-state phenyl cation. Since most phenyl cations formed by electron impact have extra internal energy, the scrambling of the carbon atoms possibly occur even if they do not give rise to fragmentation.



18

A MINDO/3 calculation on structure **18** has been performed resulting in a heat of formation 44 kcal/mol higher than **1**.[8] This structure is considered to be the acceptable intermediate of hydrogen randomization, since the scrambling could proceed by successive 1,2 shifts. Although we further tried to find out the MERP under conditions that maintain the ring structure in **1**, there was no other path. Conclusively, the activation energy of hydrogen scrambling is lower than the energies for fragmentation and is comparable to that of carbon scrambling.

Conclusion

The stabilities of the $C_6H_5^+$ system are calculated as shown in Table I. The lowest activation energy for elimination of C_2H_2 from **1** is predicted to be 108 kcal/mol. This elimination should occur through a linear structure (either **2** or **3**), which may be formed by the β-bond cleavage of **1**. On the other hand, direct loss of C_2H_2 from **1** requires ca. 118 kcal/mol. Generally the cleavage involving the β bond to the carbon atom with the formal cation is easier than the α bond. These results support the concept of the fragmentation rules in the aromatic ring system.

The energies which are required for interstructural conversions are in Table II. Those values are relatively low when compared to the energies for fragmentation, suggesting easy mutual conversion before fragmentation. The possible least energy path for 1 → 5, one of the paths of carbon scrambling, is examined to give 69 kcal/mol above **1**. This value is far lower than that of fragmentation, explaining the experimental results of the phenyl cation produced from iodobenzene by electron impact. Ease or difficulity of hydrogen migration between carbon atoms entirely depends on the structure of the ion, although hydrogen scrambling in **1** needs 44 kcal/mol.

Acknowledgment. We acknowledge Y. Nakajima (Hoshi College of Pharmacy) for technical assistance. The computations were carried out on Hitac 8800/8700 computers at the computation center of the University of Tokyo. This research was supported in part by the Ministry of Education of Japan under Grant-in-Aid (No. 467369).

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(30) Dicinson, R.; Williams, D. H. *J. Chem. Soc. B* **1971**, 249.

(31) Momigny, J. *Bull. Soc. R. Sci. Liege* **1959**, *28*, 251.

Evaluation and Prediction of the Stability of Bridgehead Olefins[1]

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Abstract: Geometries, heats of formation, heats of hydrogenation, and strain energies of bridgehead olefins and the related polycycloalkanes have been calculated by using Allinger's MM1 empirical force field program. The "olefin strain" energy (OS), defined as the difference between the strain energy of an olefin and that of its parent hydrocarbon, can be used to interpret and to predict the stability and the reactivity of bridgehead olefins. A new class of compounds has been recognized, the "hyperstable" olefins, which are *less* strained than the parent hydrocarbon and should show *decreased reactivity* because of the bridgehead location of the double bonds.

Since 1924,[2] when Bredt pointed out that double bonds tend to avoid ring junctions in camphane and pinane systems, bridgehead olefins have received special and increasing attention.[3-5] What are the limits of applicability of Bredt's rule? Extensive experimental work especially during the last decade has necessitated one refinement after another. The first systematic study by Prelog[6] on bicyclo[X.3.1]alkenones indicated that X = 5

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(1) For a preliminary report of this work, see Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R.; Maier, W. F. *J. Am. Chem. Soc.* **1979**, *101*, 7634.

(2) Bredt, J.; Thouet, H.; Schmitz, J. *Liebigs Ann. Chem.* **1924**, *437*, 1.

(3) Fawcett, F. S. *Chem. Rev.* **1950**, *47*, 219.

(4) Keese, R. *Angew. Chem.* **1975**, *87*, 568. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 528.

(5) Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41. For recent reviews, see ref 37 and Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. Becker, K. B. *Ibid.* **1980**, *36*, 1717.

(6) Prelog, V.; Barman, P.; Zimmermann, M. *Helv. Chim. Acta* **1949**, *32*, 1284. *Ibid.* **1950**, *33*, 356. Prelog, V. *J. Chem. Soc.* **1950**, 420.

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represented the smallest bicyclic system in which a bridgehead olefin could be isolated. Fawcett,[3] who introduced the more general "*S* number" ($S = X + Y + Z$) for bicyclo[*X.Y.Z*]alkenes, concluded that $S = 9$ should represent the smallest value for isolable bridgehead olefins. This rule was shown to be invalid in 1967 when Wiseman[7] and Marshall[8] reported the isolation of bicyclo[3.3.1]nonene (corresponding to $S = 7$). Since the *S* number did not distinguish between isomeric bridgehead olefins, Köbrich[9] proposed in 1973 three additional rules which allowed such distinctions to be made. As will be discussed later, two of these rules have since been violated by experimental results and even the third does not appear to be general.

The only qualitative rule still valid was suggested by Wiseman[7] in 1970. He recognized that all isolable bridgehead olefins are contained in a trans cycloalkene unit with at least eight carbon atoms. When the trans alkene-containing ring is seven or six membered, bridgehead olefins are predicted not to be observable at room temperature. Unfortunately, this trans olefin rule does not distinguish among isomeric compounds; a more detailed theory is needed.

Burkert[10] and Ermer[11] have demonstrated that the results of empirical force field calculations on bridgehead olefins correlate with experimental data, but the number of examples investigated was limited. Ermer[11] proposed a "quantitative reactivity criterion for bridgehead olefins" on the basis of "the nonplanar deformation energy V_{oop} of the double bond". We agree that nonplanar olefin deformation is important in determining behavior. Unfortunately, "V_{oop}" is not directly related to an experimentally measurable quantity and the computer program employed to obtain such values is not generaly available. Empirical force field calculations are the only computational methods which allow total optimization of all conformational isomers of larger molecules while consuming modest amounts of computer time. They also give generally reliable geometries and energies where comparisons with experiment can be made. Moreover, such calculations also permit the ready examination of systems presently unknown, unavailable, inaccessible, or experimentally impossible.

As first pointed out by Lesko and Turner,[12] the strain energy of a bridgehead olefin is a composite of the extra strain associated with the double bond and the residual strain associated with the carbon skeleton. We have adopted this conceptual framework and in a preliminary communication proposed that this extra strain associated with the double bond, abbreviated as OS (olefinic strain), could be used as an index of bridgehead olefin stability.[1] "Strain energies" are defined quantities easily derivable from experimental or from calculated heats of formation.[13,14] "Olefinic strain" is directly related to heats of hydrogenation; new gas-phase measurements of $\Delta H_{\mathrm{H}}°$ of bridgehead olefins[15] which became available after our calculations were completed allow our results to be evaluated. We now present the results of an extensive survey of known and unknown bridgehead olefins by force field methods.[14]

Calculational Procedures

Olefinic strain (OS) is calculated (we have used Allinger's MM1 force field)[14a] by subtracting the total strain energy of the most stable conformer of the parent hydrocarbon from the total strain energy of the olefin, also in the most stable conformation. Although the preferred conformations of an olefin and the related polycycloalkane are not necessarily the same, this is a realistic definition of OS, since it relates to the change in energy which accompanies chemical reactions such as hydrogenation. Since OS values are obtained by subtraction, errors inherent in the calculations should tend to cancel. The force field parameterizations for alkanes and alkenes only differ at the olefinic site.

The MM1 program also calculates heats of formation, from which the strain energies are derived.[14] The difference between the heat of formation of an olefin and that of its parent alkane represents the heat of hydrogenation, $\Delta H_{\mathrm{H}}°$, a quantity directly measurable under favorable experimental circumstances.[15] However, heats of hydrogenation depend upon the degree of substitution of an olefin. When this differs from system to system, $\Delta H_{\mathrm{H}}°$ does not provide a direct comparison of the extra strain associated with an olefin. However, most bridgehead olefins studied to date are trisubstituted. For these, OS and $\Delta H_{\mathrm{H}}°$ are related by a constant difference, 26.1 kcal/mol (the heat of hydrogenation of a hypothetical unstrained trisubstituted olefin to the hypothetically unstrained alkane). $\Delta H_{\mathrm{H}}°$'s can be calculated from data in Table I.

For the smaller systems, our definition of OS does not create practical problems in carrying out calculations, since possible conformations are limited in number. For the larger systems great care has to be employed to ensure that the most stable conformations have been found.

This means that many trial geometries have to be examined. Some of these are converted to other conformations on optimization; others give higher energy local minima. As with all such potential energy surface scans, minima can be identified, but there is no rigorous way to demonstrate that the *global minimum* has been located. We have searched widely and believe these global minima have been found. One of the earlier studies was not always successful in this respect.[10] Our lowest energy conformations agree with those given by Ermer.[11]

Table I summarizes data on all bridgehead olefins examined; results on the corresponding polycycloalkanes are included. All bicycloalkene isomers with nine or fewer carbons have been calculated. However, bridgehead olefins containing three-membered rings have been omitted, since the force field programs employed have not been parameterized satisfactorily for cyclopropane rings. Since the number of possible conformations increase rapidly with the size of the polycyclic system, only selected examples of the larger molecules up to 14 carbon atoms were studied. All experimentally reported bridgehead olefins are included.

Table II summarizes the conformational isomers (minima on the potential energy surface) of the bridgehead olefins as well as the parent hydrocarbons. Many of the larger bicyclic isomers, with eight or more carbon atoms, prefer strongly twisted conformations. (For representational clarity, this twisting is not shown in the drawings in Table II which designate the general geometrical features of each species.) All important minimum energy conformations are given, but Table II does not indicate all the trial geometries which were examined. Many of these proved not to represent energy minima and were converted to another conformation automatically during the structure optimization routines inherent in the computer program employed. Especially with the larger bicycloalkanes only the most likely conformations were taken into account.

Conformations

Although not the main purpose of this paper, some general comments on the conformational preferences found are in order.[14c] For the parent hydrocarbons (Table II), some common conformational features are discernible. Four- or five-membered rings tend to be puckered. If a six-membered ring connected 1,3 is present, the most stable chair conformation dominates and controls the geometry of the rest of the molecule. This holds through all examples and is illustrated by bicyclo[3.2.1]octane (**14a**), where

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(7) Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956. Wiseman, J. R. *Ibid.* **1967**, *89*, 5966.

(8) Marshall, J. A.; Faubl, H. *J. Am. Chem. Soc.* **1970**, *92*, 948. *Ibid.* **1967**, *89*, 5964.

(9) Köbrich, G. *Angew. Chem.* **1973**, *85*, 494. *Angew. Chem., Int. Ed. Engl.*, **1973**, *12*, 464.

(10) Burkert, U. *Chem. Ber.* **1977**, *110*, 773.

(11) Ermer, O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 837.

(12) Lesko, P. M.; Turner, R. B. *J. Am. Chem. Soc.* **1968**, *90*, 6888.

(13) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

(14) (a) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579. Allinger, N. L.; Sprague, J. T. *Ibid.* **1975**, *31*, 21. Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. QCPE Program No. 318 (MM1). (b) MM2: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (c) There have been numerous calculational studies of the conformations of polycyclic systems. See Ōsawa, E.; Aigami, K.; Inamoto, T. *J. Chem. Soc. Perkin Trans. 2* **1979**, 172 and references cited therein.

(15) Lennartz, H. W., Dissertation, Bochum, 1979. Cf. Roth, W. R.; Lennartz, H. W. *Chem. Ber.* **1980**, *113*, 1806.

the seven-membered ring is forced to assume a boat conformation in favor of the six-membered ring chair. A 1,4 connection forces a six-membered ring into a boat structure, but in all bicyclo[2.2.*n*]alkanes ($n \geq 2$), the six-membered ring is twisted, often quite strongly.

Seven-membered rings try to attain a chair conformation, as seen in **18a**, **27a**, **40a**, and also **50a**. Exceptions can be noted. Bicyclo[3.3.2]decane (**34a**) has one seven-membered ring in its least-strained chair in its least-strained chair conformation, whereas the second seven-membered ring is forced to assume a boat conformation because of the transannular hydrogen repulsion.[14c] Eight-membered ring conformations in bicyclic systems are too complex for simple generalization. In the systems investigated, larger rings normally adapt their geometry to favor the best conformations of the smaller ring provided the latter is at least six membered. A strong preference for the first of the two types of axial bridging of a 1,3-connected seven-membered ring is also noteworthy.

The bridgehead olefins follow quite different conformational rules. The dominating influence is the strain associated with the double bond. Without exception, the smaller of the two olefinic rings incorporates a cis cycloalkene, whereas the larger ring is thus forced into a trans configuration. If the double bond is located in one of the larger bicycloalkene bridges, the following decreasing conformational influence is found: cis cyclopentene > cis cyclohexene > cis cycloheptene > cis cyclooctene > chair cyclohexane > chair cycloheptene > chair cyclooctane (the last two can be dominated by transannular repulsion effects).

Comparison of OS Values with Experimental Behavior

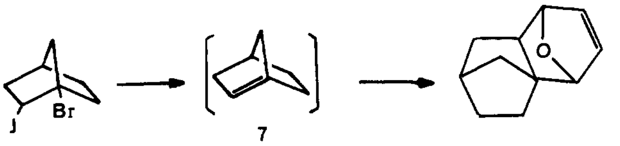
The following *empirical* rules, deduced from comparison of OS values with experimental data, allow classification of individual bridgehead olefins into three groups:

isolable bridgehead olefins	OS ≤ 17 kcal/mol
observable bridgehead olefins	17 kcal/mol ≤ OS ≤ 21 kcal/mol
unstable bridgehead olefins	OS ≥ 21 kcal/mol

These categories, loosely defined as follows, refer to condensed-phase observations. "Isolable" olefins are kinetically stable at room temperature, at least long enough to permit reactions, spectroscopic measurements, etc. to be carried out. "Observable" olefins are not isolable at room temperature but may be detected at lower temperatures spectroscopically. "Unstable" olefins are not spectroscopically observable at low temperatures, except perhaps in matrix isolation. They are commonly detected by trapping experiments. These rules are illustrated by the following examples; particular reference is made to the latest literature. A general discussion of the limitations of these rules will follow.

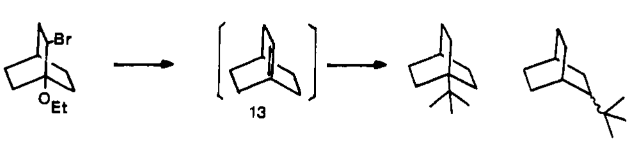
Discussion

Bicyclo[2.2.1]hept-1-ene (**7**), the smallest bridgehead olefin which has been investigated experimentally, has been trapped with furan.[16] As it is consistent with its high OS value, 34.9 kcal/mol, **7** has not been observed directly.



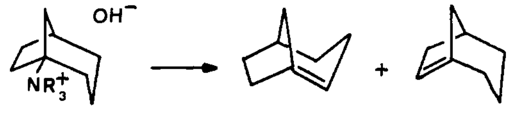
7

Bicyclo[2.2.2]oct-1-ene (**13**), with OS = 40.4 kcal/mol, also is not observable; its existence has been established by trapping experiments.[17]



13

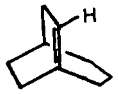
Bicyclo[3.2.1]oct-1-ene (**15a**) (OS = 28.6 kcal/mol) and bicyclo[3.2.1]oct-1(7)-ene (**16a**) (OS = 27.2 kcal/mol) are both indicated by Diels–Alder trapping products to have been formed in small amounts from pyrolysis of the trimethylammonium hydroxide.[18] **16a** has also been formed by an intramolecular Wittig reaction, but attempts to prepare **7** by a similar reaction failed.[19] These results are not surprising; **7** has almost 8 kcal/mol more olefinic strain energy than **16a**.



15a 16a

Bicyclo[3.2.2]non-1-ene (**22**) (OS = 19.5 kcal/mol) and bicyclo[3.2.2]non-1(7)-ene (**23a**) (OS = 20.6 kcal/mol) represent the smallest observable bicyclic bridgehead olefins reported to date. They have been investigated at −80 °C[20] but dimerize upon warming to higher temperatures. The more abundant isomer reacts more rapidly. The 2:1 statistical advantage evidentally favors the formation of **23a** kinetically; the larger OS value indicates **23a** to be less stable than **22**.

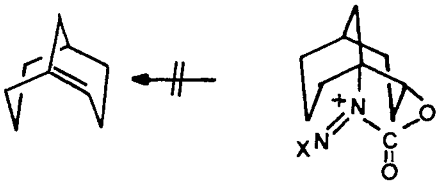
22



23a

We do not agree with Burkert,[10] who asserted that the reliability of force field calculations decreases when applied to strained hydrocarbons like **16a** and **23a**. Burkert, who also used the Allinger MM1 program,[14a] did not make use of the "olefinic strain" concept but only compared the total strain values. Since **16a** and **23a** show almost identical total strain energies, he concluded that these olefins should have been comparably stable, contrary to experiment. Comparison of OS values (27.5 vs. 35.6 kcal/mol for **23a** and **16a**, respectively) leads to different interpretation. The value for **16a** is about 8 kcal/mol greater than that of **23a**; the latter olefin, but not **16a**, has been observed.

The most widely investigated stable bridgehead olefin, bicyclo[3.3.1]non-1-ene (**25a**), has an OS value of 15.2 kcal/mol. Experimental estimates of the strain energy associated with the double bond are about 12 kcal/mol,[12,15] not far from the calculated value. The chemistry of **25a** has been reviewed.[7,8] Remarkable is the addition of bromine and the very rapid addition of acids. This enhanced reactivity in acidic media points to a high-energy HOMO as expected for deformed olefins. An interesting experiment has been carried out by White et al.,[21] who prepared **25a** from the cis precursor **84a**. In contrast, all attempts to convert the trans precursor **84b** into **25c** failed. The conclusion that the *E* form **25c** is much more strained than the *Z* form **25a** is con-



25c 84b

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(16) Keese, R.; Krebs, E. P. *Angew. Chem.* **1971**, *83*, 254. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 262.

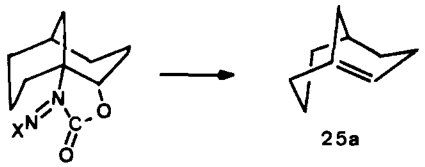
(17) Grootveld, H. H.; Blomberg, C.; Bickelhaupt, F. *J. Chem. Soc., Chem. Commun.* **1973**, 542. Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8209.

(18) Chong, J. A.; Wiseman, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 8627.

(19) Dauben, W. G.; Robbins, J. D. *Tetrahedron Lett.* **1975**, 151.

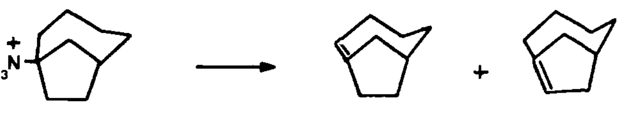
(20) Wiseman, J. R.; Chong, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 7775.

(21) Kim, M.; White, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 1172.


84a 25a

firmed by the OS values, 44.2 kcal/mol for **25c** compared to 15.2 kcal/mol for **25a**. Quite recently, Becker et al. developed a simple gas-phase procedure which makes **25a** as well as **24a** and **28a** readily available.[22] Another experimental value for **25a** has recently determined, the heat of hydrogenation $\Delta H_{\mathrm{H}}^{\circ}$.[15] The value, −37.9 kcal/mol, is not in as good agreement as one would like with the calculated $\Delta H_{\mathrm{H}}^{\circ}$ (**25a** → **24a**) = −41.2 kcal/mol. However, the MM2 force field[14b] gives a similar $\Delta H_{\mathrm{H}}^{\circ}$ value, 41.7 kcal/mol. In such discrepancies between calculated and experimental data, the former not always are at fault.

From the common precursor, **85**, predominant production of bicyclo[4.2.1]non-1(8)-ene (**29a**) compared to bicyclo[4.2.1]non-1-ene (**28a**) was observed by Wiseman et al.[23] In the absence of more sophisticated methods, molecular models indicated that **29a** should be the less stable isomer; this conclusion required a complicated rationalization of the experimental facts. In contrast, the OS values indicate **29a** (OS = 9.1 kcal/mol) to be much more stable than **28a** (OS = 14.1 kcal/mol) and provide a simple explanation of the product distribution (as has already been recognized).[10,11] The X-ray structure of the metal complex shows a twisted arrangement.[24] For **28a** as well as for **29a**, $\Delta H_{\mathrm{H}}^{\circ}$'s have been measured.[15] The experimental values of −36.3 and −42.0 kcal/mol, respectively, correspond well with the calculated ones, −35.2 and −40.2 kcal/mol. An indirect experimental strain estimate of 20–22 kcal/mol for a derivative of **30a** agrees with the OS value of 21.6 kcal/mol.[25]



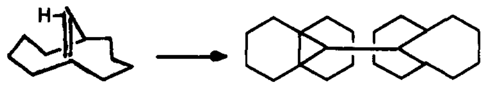
85 28a 29a

Bicyclo[5.1.1]non-1-ene (**32a**)(OS = 17.5 kcal/mol) is less stable than bicyclo[5.1.1]non-1(8)-ene (**33**) (OS = 14.5 kcal/mol); bicyclo[3.3.2]dec-1-ene (**35a**) (OS = 4.7 kcal/mol) is more stable than bicyclo[3.3.2]dec-1(9)-ene (**36a**) (OS = 18.9 kcal/mol). These results are consistent with calculations of Ermer[11] and with experimental data.[26]

Bicyclo[4.2.2]dec-1-ene (**38a**) (OS = 8.2 kcal/mol) and bicyclo[4.2.2]dec-1(8)-ene (**39a**) (OS = 7.9 kcal/mol) are both isolable.[27] The same is true for the unstrained bicyclo[4.3.1]dec-1-ene (**41a**) (OS = 2.5 kcal/mol) and bicyclo[4.3.1]dec-1(9)-ene (**42a**) (OS = 3.0 kcal/mol), which were formed in the same experiment.[28] **41a** has also been prepared by an intramolecular Diels–Alder reaction.[29]

Bicyclo[4.4.1]undec-1-ene (**51a**) (OS = −1.5 kcal/mol) has also been isolated;[30] the negative value indicates that **51a** should be *less reactive* than unstrained olefins. In contrast, bicyclo[4.4.1]undec-1(11)-ene (**52a**) (OS = 22.3 kcal/mol) dimerized and could only be trapped by cycloaddition.[30]

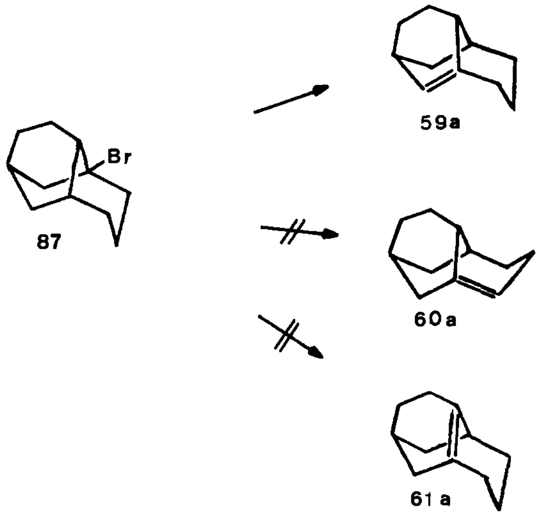
Norboran-7-ylidene (**86**) rearranges to the isolable bicyclo[3.2.0]hept-1-ene (**70**) (OS = 13.9 kcal/mol).[31] 3-Homoadamantane (tricyclo[4.3.1.$1^{3,8}$]undec-3-ene) (**65**) has been observed at −80 °C;[1] this is consistent with the OS value of 20.2 kcal/mol. **65** is known to dimerize at higher temperatures.[32]


52a


86 70

Adamantene (**63**) (OS = 39.5 kcal/mol), the most intensively investigated unstable bridgehead olefin,[33] has only recently been directly detected in a matrix experiment.[34]

Dehydrobromination of 3-bromotricyclo[5.3.1.$0^{3,8}$]undecane (**87**) yielded exclusively tricyclo[5.3.1.$0^{3,8}$]undec-2(3)-ene (**59a**)[35] (OS = 12.5 kcal/mol). The isomeric olefins **60a** (OS = 15.3) and **61a** (OS = 38.8) have not been observed.



59a 87 60a 61a

Köbrich's Rules

Because of the complexity and large number of possible organic systems, we believe that only quantitative calculational procedures will survive the rigors of extensive comparison with experimental results. In contrast, the conventional view favors generalizations cast in terms of qualitative rules. The most detailed of these pertaining to bridgehead olefins were formulated by Köbrich in 1971. Let us examine the present status of Köbrich's rules.[9] For each, violations either are known experimentally or are predicted on the basis of our calculations.[1] (Köbrich's simplified notation is employed below.[9] Thus, "44$\bar{1}$" refers to bicyclo[4.4.1]undec-1(11)-ene (**52**); the bridgehead double bond extends to the one-atom bridge.)

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(22) Becker, K. B.; Pfluger, R. W. *Tetrahedron Lett.* **1979**, 3713.

(23) Wiseman, J. R.; Chan, H. F.; Ahola, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 2812.

(24) Stamm, E.; Becker, K. B.; Engel, P.; Ermer, O.; Keese, R. *Angew. Chem.* **1979**, *91*, 746. *Angew Chem., Int. Ed. Engl.* **1979**, *18*, 685.

(25) Warner, P.; LaRose, R.; Lee, C.; Clardy, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 7607.

(26) Wiseman, J. R., private communication to O. Ermer, cited in ref 11.

(27) Sy, A. O. Ph.D. Dissertation, University of Michigan, 1977.

(28) Gassman, P. G.; Lein, G. M., Jr.; Yamaguchi, R. *Tetrahedron Lett.* **1976**, 3113.

(29) Shea, K. J.; Wise, S. *Tetrahedron Lett.* **1979**, 1011. *J. Am. Chem. Soc.* **1978**, *100*, 6519.

(30) Becker, K. B.; Chappuis, J. L. *Helv. Chim. Acta* **1979**, *62*, 34.

(31) Moss, R. A.; Whittle, J. R. *J. Chem. Soc., Chem. Commun.* **1969**, 341.

(32) Farcasiu, M.; Farcasiu, D.; Conlin, R. T.; Jones, M., Jr.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8207.

(33) Lenoir, D. *Tetrahedron Lett.* **1972**, 4049. Lenoir, D.; Firl, J. *Liebigs Ann. Chem.* **1974**, 1467. Alberts, A. H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1973**, 3047. Gano, J. E.; Eizenberg, L. *J. Am. Chem. Soc.* **1973**, *95*, 972. Burns, W.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1974**, 858. Adams, B. L.; Kovacic, P. *J. Am. Chem. Soc.* **1974**, *96*, 7014. Burns, W.; Grant, D.; McKervey, M. A.; Step, G. *J. Chem. Soc., Perkin Trans 1* **1976**, 234. Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 2896. Schwartz, H.; Reetz, M. T.; Maier, W. F.; Wesdemiotis, C.; Chatziiosifidis, I.; Schilling, M. *Angew. Chem.* **1979**, *91*, 1019. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 952. Cadogan, J. I. G.; Leardini, R. *J. Chem. Soc. Chem. Commun.* **1979**, 783. Lenoir, D.; Kornrumpf, V.; Fritz, H. P. *Angew. Chem.*, in press.

(34) Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637.

(35) Takaishi, N.; Fujikura, Y.; Inamoto, Y.; Ikeda, H.; Aigami, K. *J. Chem. Soc., Chem. Commun.* **1975**, 371.

Köbrich's Rule A. "For homologs with different *S* values (see introduction for definition of Fawcett's *S*), the ring strain varies inversely with *S*."

Experimental violations: $44\bar{1}$ ($S = 9$) is not observable, but $\bar{3}31$, $\bar{4}21$, $4\bar{2}1$, $\bar{5}11$, and $5\bar{1}1$ (all with $S = 7$) and $\bar{3}32$, $\bar{4}22$, $4\bar{2}2$, $\bar{4}31$, and $4\bar{3}1$ (all with $S = 8$) are stable.

Predicted violations: in contrast to the above $S = 7$ cases, $43\bar{1}$ and $33\bar{2}$ (both with $S = 8$) are indicated by calculation to be unstable.

Köbrich's Rule B. "For a given *S*, the ring strain varies inversely with the size of the larger of the two rings with respect to which the bridgehead double bond is endocyclic."

Predicted violations: $32\bar{1}$ ($S = 6$, with a *trans*-cyclohexene) is less strained than $4\bar{1}1$ ($S = 6$, *trans*-cycloheptene).

Köbrich's Rule C. "For a given bicyclic skeleton, the ring strain varies inversely with the size of the bridge containing the bridgehead bond."

Experimental violations: $\bar{4}21 > 4\bar{2}1$ and $\bar{5}11 > 5\bar{1}1$ in ease of formation.

Predicted violations: $\bar{4}22 > 4\bar{2}2$ and $\bar{2}11 > 2\bar{1}1$ strain energy order.

Table III provides a systematic summary of bridgehead olefin OS values. Although a trend to lower values from top left to lower right may be noted, the many irregularities present obstacles to the formulation of qualitative rules.

Predictions

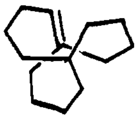
We make the following predictions concerning the stability of bridgehead olefins.

According to the calculated OS values (21.0 kcal/mol), bicyclo[1.1.1]pent-1-ene (**2**) might be observable. However, the MM1 force field has not been parameterized for such highly strained compounds and may not give reliable results for such an extreme case. Bicyclo[4.2.1]non-1(9)-ene (**30a**) should be unstable at room temperature but observable at low temperatures (OS = 21.6 kcal/mol). Bicyclo[4.3.1]dec-1(9)-ene **42a** (OS = 3.0 kcal/mol) should be a normal olefin whereas its isomer **43a** (OS = 22.0 kcal/mol) should only be observable at low temperatures.

Bicyclo[3.3.3]undec-1-ene (**45a**) (OS = 3.9 kcal/mol) should be a stable olefin. This low OS value is remarkable, since **45a** still contains a trans cyclooctene unit. The indicated stability of **45a** as well as that of **35a** may be ascribed to the known tendency of bridgehead atoms of bicyclo[3.3.3]undecanes (and similar polycyclic systems incorporating middle rings) to favor sp^2 configurations, e.g., as has been shown by the rapid solvolysis of 1-chloro[3.3.3]undecane.[36]

A new class of "hyperstable" olefins can now be defined, olefins which contain *less* strain than that of the parent hydrocarbon and have *negative* OS values. Such olefins should be very *unreactive*—not due to steric hindrance[37] or to enhanced π-bond strength but due to special stability afforded by the cage structure of the olefin and to the greater strain of the parent polycycloalkane. As mentioned above, the known[30] bicyclo[4.4.1]undec-1-ene (**51a**) (OS = −1.5 kcal/mol) should be a borderline example of this type.

Bicyclo[4.3.2]undec-1-ene (**47a**) (OS = −5.4 kcal/mol), bicyclo[4.3.2]undec-1(9)-ene (**48a**) (OS = −7.2 kcal/mol), and bicyclo[4.4.2]dodec-1-ene (**54a**) (OS = −13.0 kcal/mol) represent three members of this new class. An even more impressive example is bicyclo[4.4.4]tetradec-1-ene (**57a**), with an OS value of −14.1 kcal/mol. This corresponds to a heat of hydrogenation of only 12 kcal/mol. Therefore, **57a** should be an unusually unreactive olefin and may even resist hydrogenation under normal conditions. Some monocyclic middle ring olefins can also be classified as "hyperstable", but the lowest heat of hydrogenation which has been reported is 20.7 kcal/mol (for cis cyclodecene).[38] Polycyclic systems magnify such middle ring effects.[36,39]



57a

Correlation of Thermodynamic Stability and Reactivity

Empirical force field calculations refer to the ground state and only reflect thermodynamic stability. Chemical reactivity is related to the differences in energy between ground and transition states. Transition-state energies have not been taken into account in our analysis. What then is the reason for the surprising correlation between thermodynamic stability and chemical reactivity we have noted? Segal's calculated transition state for 2 + 2 dimerization of two ethylenes to give cyclobutane indicated highly twisted, pyramidalized structures for the olefinic moieties.[40a] The olefin geometries of highly strained bridgehead double bonds closely resemble these distorted ethylene dimerization transition states. The ground-state geometries of highly strained bridgehead olefins (and the resulting diradicaloid character) may thus facilitate dimerizations of various types; this helps to rationalize the observed correlation of the OS values with chemical reactivity.

A similar conclusion results from simple MO arguments. A twisted olefin has reduced π overlap. This results in an increase of the HOMO energy and a simultaneous decrease of the LUMO energy. HOMO–LUMO degeneracy is reached when the twist angle becomes 90° (D_{2d} symmetry). Since the OS values mostly reflect the twisting strain of the olefin, there should be a rough proportionality with the decrease in the HOMO–LUMO gap. The correlation of OS with chemical reactivity can thus be interpreted on the basis of frontier orbital theory.

A reviewer has pointed out that the measured ionization potentials of some isolable bridgehead olefins (OS = 9–14 kcal/mol)[40b] are "essentially normal". This behavior is to be expected. Only part of the total olefinic strain is localized at the double bond and is reflected in changes in HOMO energies.

OS values should reveal trends even though the values may not be accurate for the more strained systems. MM1 has *not* been parameterized with experimental thermochemical data for such unstable compounds. Newer force fields which have been parameterized for cage systems, e.g., MM2,[14b] may give better results.

Violations

Are these rules applicable to other types of strained olefins? Unfortunately, not always. Olefins lacking *twisted* geometries, e.g., cyclopropenes, do not obey the bridgehead olefin OS rules. Despite very high OS values, such olefins are isolable. Olefins with double bonds located between two bridgehead positions, termed "zero-bridge olefins", are generally not considered to be Bredt olefins.[3] All known bicyclic zero-bridge olefins, like bicyclo[2.2.0]hex-1(4)-ene (**68**), should have essentially planar arrangements around the double bond (but may have unusually low out-of-plane bending force constants).[41] In contrast to the twisted bridgehead olefins already considered, the energy separation of the frontier MO's of zero-bridge olefins, cyclopropenes, and similar olefins should be essentially unaffected by the strain in the σ skeleton of the molecule. This σ strain is responsible for the OS values calculated but is less directly related to olefinic reactivity.

A revealing example is provided by **68**. If our OS rules were to be followed, the OS value (31 kcal/mol) would indicate that observation should not be possible. Instead, **68** is known to be stable at low temperatures, although above −25 °C rapid polymerization occurs.[42] Bicyclo[3.2.0]hept-1(5)-ene (**72**) (OS = 20.5

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(36) Parker, W.; Tranter, R. L.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121.

(37) Reviewed in Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. Greenberg, A.; Liebman, J. F. "Strained *Organic Molecules*"; Academic Press: New York, 1978.

(38) (a) Jensen, J. L. *Prog. Phys. Org. Chem.* **1976**, *12*, 189. (b) White, D. N. J.; Bovill, M. J. *J. Chem. Soc., Perkin Trans II*, **1977**, 1610.

(39) Alder, R. W.; Arrowsmith, R. J. *J. Chem. Res.* **1980**, 163.

(40) (a) Segal, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 7892. (b) Batich, C.; Ermer, O.; Heilbronner, E.; Wiseman, J. R. *Angew. Chem.* **1973**, *85*, 302. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 312.

(41) Wagner, H.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 1210.

Table I. Calculated Energies (kcal/mol) for Olefins and Parent Hydrocarbons[a]

system	ΔH_f°	strain energy	relative energy	OS
bicyclo[1.1.1]pentane (1)	68.45	85.67		
bicyclo[1.1.1]pentene (2)	115.58	106.71		21.0
bicyclo[2.1.1]hexane (3)	18.33	41.14		
bicyclo[2.1.1]hex-1-ene (4)	69.43	66.15		25.0
bicyclo[2.1.1]hex-1(5)-ene (5)	77.64	74.36		33.2
bicyclo[2.2.1]heptane (6)	−13.27	15.11		
bicyclo[2.2.1]hept-1-ene (7)	47.67	49.97		34.9
bicyclo[2.2.1]hept-1(7)-ene (8)	51.27	53.58		38.5
bicyclo[3.1.1]heptane (9)	5.98	34.37		
bicyclo[3.1.1]hept-1-ene (10)	60.92	63.22		28.9
bicyclo[3.1.1]hept-1(6)-ene (11)	71.21	73.51		39.1
bicyclo[2.2.2]octane (12)	−23.76	10.21		
bicyclo[2.2.2]oct-1-ene (13)	42.72	50.60		40.4
bicyclo[3.2.1]octane (14a)	−23.63	10.34	0.0	
(14b)	−17.18	16.79	6.45	
bicyclo[3.2.1]oct-1-ene (15a)	31.03	38.92	0.0	28.6
(15b)	44.66	52.55	13.63	
bicyclo[3.2.1]oct-1(7)-ene (16a)	29.64	37.52	0.0	27.2
(16b)	31.57	39.45	1.87	
bicyclo[3.2.1]oct-1(8)-ene (17a)	39.18	47.07	0.0	36.7
(17b)	43.29	51.17	4.10	
bicyclo[4.1.1]octane (18a)	−1.24	32.73	0.0	
(18b)	7.59	41.56	8.83	
bicyclo[4.1.1]oct-1-ene (19a)	59.86	67.75	0.0	35.0
(19b)	60.50	68.39	0.64	
bicyclo[4.1.1]oct-1(7)-ene (20a)	61.62	69.51	0.0	37.8
(20b)	65.83	73.72	4.21	
bicyclo[3.2.2]nonane (21)	−24.63	14.92		
bicyclo[3.2.2]non-1-ene (22)	21.06	34.53		19.5
bicyclo[3.2.2]non-1(7)-ene (23a)	22.17	35.64	0.0	20.6
(23b)	36.67	50.14	14.50	
bicyclo[3.3.1]nonane (24a)	−30.52	9.04	0.0	
(24b)	−28.39	11.17	2.13	
(24c)	−23.26	16.29	7.25	
bicyclo[3.3.1]non-1-ene (25a)	10.72	24.20	0.0	15.2
(25b)	11.91	25.38	1.18	
(25c)	39.75	53.22	29.02	
(25d)	43.09	56.56	32.36	
bicyclo[3.3.1]non-1(9)-ene (26a)	43.77	57.24	0.0	48.2
(26b)	45.01	58.49	1.25	
(26c)	48.27	61.74	4.50	
bicyclo[4.2.1]nonane (27a)	−23.68	15.88	0.0	
(27b)	−17.00	22.56	6.68	
bicyclo[4.2.1]non-1-ene (28a)	16.55	30.00	0.0	14.1
(28b)	16.87	30.34	0.34	
(28c)	45.59	59.06	29.06	
bicyclo[4.2.1]non-1(8)-ene (29a)	11.51	24.98	0.0	9.1
(29b)	14.31	27.79	2.81	
bicyclo[4.2.1]non-1(9)-ene (30a)	24.04	37.51	0.0	21.6
(30b)	45.27	58.74	21.23	
(30c)	51.34	64.82	27.31	
bicyclo[5.1.1]nonane (31a)	−0.82	38.73	0.0	
(31b)	2.36	41.92	3.19	
bicyclo[5.1.1]non-1-ene (32a)	42.74	56.21	0.0	17.5
(32b)	45.00	58.47	2.26	
bicyclo[5.1.1]non-1(8)-ene (33)	39.74	53.21		14.5
bicyclo[3.3.2]decane (34a)	−24.64	20.50	0.0	
(34b)	−24.25	20.89	0.39	
(34c)	−22.03	23.11	2.61	
bicyclo[3.3.2]dec-1-ene (35a)	6.19	25.24	0.0	4.7
(35b)	10.13	29.19	3.95	
(35c)	20.71	39.77	14.53	
(35d)	43.03	62.09	37.85	
bicyclo[3.3.2]dec-1(9)-ene (36a)	20.40	39.46	0.0	18.9
(36b)	25.21	44.27	4.81	
(36c)	31.59	50.65	11.19	
bicyclo[4.2.2]decane (37a)	−24.79	20.35	0.0	
(37b)	−20.02	25.12	4.77	
bicyclo[4.2.2]dec-1-ene (38a)	9.45	28.51	0.0	8.2
(38b)	12.85	31.91	3.40	
bicyclo[4.2.2]dec-1(8)-ene (39a)	9.19	28.24	0.0	7.9
(39b)	9.53	28.58	0.34	
(39c)	11.22	30.27	2.03	
bicyclo[4.3.1]decane (40a)	−30.50	14.64	0.0	
(40b)	−30.02	15.11	0.47	
(40c)	−27.69	17.45	2.81	
(40d)	−27.29	17.84	3.20	
(40e)	−23.88	21.26	6.62	

Table I (*Continued*)

system	$\Delta H_f°$	strain energy	relative energy	OS
bicyclo[4.3.1]dec-1-ene (41a)	−1.95	17.11	0.0	2.5
(41b)	−1.51	17.55	0.44	
(41c)	0.11	19.16	2.05	
(41d)	3.34	22.39	5.28	
bicyclo[4.3.1]dec-1(9)-ene (42a)	−1.46	17.60	0.0	3.0
(42b)	−0.89	18.17	0.57	
(42c)	3.97	23.03	5.43	
(42d)	35.68	54.73	37.13	
(42e)	36.16	55.21	37.61	
(42f)	40.39	59.45	41.85	
bicyclo[4.3.1]dec-1(10)-ene (43a)	17.58	36.63	0.0	22.0
(43b)	39.46	58.52	21.89	
(43c)	41.14	60.19	23.56	
(43d)	42.21	61.27	24.64	
(43e)	42.61	61.66	25.03	
(43f)	45.05	64.11	27.48	
(43g)	45.88	64.94	28.31	
bicyclo[3.3.3]undecane (44a)	−21.69	29.03	0.0	
(44b)	−8.12	42.61	13.58	
bicyclo[3.3.3]undec-1-ene (45a)	8.26	32.90	0.0	3.9
(45b)	36.79	61.42	28.52	
bicyclo[4.3.2]undecane (46a)	−19.60	31.12	0.0	
(46b)	−18.18	31.93	0.81	
(46c)	−16.01	34.71	3.59	
(46d)	−15.19	35.53	4.41	
bicyclo[4.3.2]undec-1-ene (47a)	1.05	25.69	0.0	−5.4
(47b)	1.23	25.87	0.18	
(47c)	7.82	32.46	6.77	
(47d)	9.71	34.35	8.66	
bicyclo[4.3.2]undec-1(9)-ene (48a)	−0.76	23.88	0.0	−7.2
(48b)	0.51	25.15	1.27	
(48c)	21.68	46.32	22.44	
bicyclo[4.3.2]undec-1(10)-ene (49a)	7.88	32.52	0.0	1.4
(49b)	9.43	34.07	2.55	
(49c)	12.02	36.66	4.14	
(49d)	39.79	64.43	31.91	
(49e)	41.83	66.47	33.95	
(49f)	42.57	67.21	35.69	
(49g)	48.24	72.88	40.36	
bicyclo[4.4.1]undecane (50a)	−33.52	17.20	0.0	
(50b)	−28.99	21.73	4.53	
(50c)	−27.34	23.39	6.19	
(50d)	−26.71	24.02	6.82	
(50e)	−26.43	24.29	7.09	
bicyclo[4.4.1]undec-1-ene (51a)	−8.95	15.69	0.0	−1.5
(51b)	−7.49	17.15	1.46	
(51c)	−6.73	17.91	2.22	
(51d)	−6.60	18.04	2.35	
(51e)	32.95	57.59	41.90	
bicyclo[4.4.1]undec-1(11)-ene (52a)	14.85	39.49	0.0	22.3
(52b)	17.38	42.02	2.53	
(52c)	19.29	43.93	4.44	
(52d)	40.73	65.01	26.52	
(52e)	42.09	66.73	27.24	
bicyclo[4.4.2]dodecane (53a)	−17.75	38.56	0.0	
(53b)	−14.19	42.12	3.56	
(53c)	−5.50	50.80	12.24	
bicyclo[4.4.2]dodec-1-ene (54a)	−4.70	25.53	0.0	−13.0
(54b)	2.15	32.37	6.84	
(54c)	12.82	43.05	17.52	
(54d)	16.66	46.89	21.36	
bicyclo[4.4.2]dodec-1(11)-ene (55a)	13.28	43.51	0.0	5.0
(55b)	13.56	45.78	0.27	
(55c)	48.28	78.50	34.99	
bicyclo[4.4.4]tetradecane (56a)	−7.00	60.48	0.0	
(56b)	1.12	68.56	8.08	
(56c)	1.56	69.03	8.55	
bicyclo[4.4.4]tetra-1-decene (57a)	5.01	46.40	0.0	−14.1
(57b)	7.37	48.76	2.36	
tricyclo[5.3.1.$0^{3,8}$]undecane (58a)	−29.41	13.01	0.0	
(58b)	−23.88	18.54	5.53	
tricyclo[5.3.1.$0^{3,8}$]undec-2(3)-ene (59a)	9.14	25.47	0.0	12.5
(59b)	11.37	27.71	2.24	
tricyclo[5.3.1.$0^{3,8}$]undec-3(4)-ene (60a)	12.05	28.34	0.0	15.3
(60b)	43.83	60.16	31.82	
tricyclo[5.3.1.$0^{3,8}$]undec-3(8)-ene (61a)	33.27	51.82	0.0	38.7
(61b)	41.57	60.12	8.30	

Table I (*Continued*)

system	ΔH_f°	strain energy	relative energy	OS
adamantane (**62**)	−33.34	3.49		
adamantane (**63**)	32.36	43.00		39.5
homoadamantane (**64**)	−27.37	15.05		
homoadamant-3-ene (**65**)	18.92	35.26		20.2
bicyclo[2.2.0]hexane (**66**)	27.42	50.23		
bicyclo[2.2.0]hex-1-ene (**67**)	84.47	81.19		31.0
bicyclo[2.2.0]hex-1(4)-ene (**68**)	82.43	81.37		31.1
bicyclo[3.2.0]heptane (**69**)	4.46	32.85		
bicyclo[3.2.0]hept-1-ene (**70**)	44.47	46.77		13.9
bicyclo[3.2.0]hept-1(7)-ene (**71**)	47.27	49.57		16.7
bicyclo[3.2.0]hept-1(5)-ene (**72**)	48.86	53.38		20.5
bicyclo[3.3.0]octane (**73**)	−21.49	12.48		
bicyclo[3.3.0]oct-1(5)-ene (**74**)	5.76	15.87		3.4
bicyclo[3.3.0]oct-1-ene (**75**)	8.93	16.82		
tricyclo[3.3.3.0^{2,6}]undecane (**76**)	−14.06	28.36		
tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene (**77**)	30.94	49.49		21.1
tricyclo[3.3.0^{3,7}]decane (**78**)	−16.71	20.13		
tricyclo[3.3.2.0^{3,7}]dec-1-ene (**79**)	31.38	44.35		24.2
tricyclo[3.3.2.0^{3,7}]dec-9(10)-ene (**80**)	11.48	20.01		−0.1
tricyclo[3.3.2.0^{3,7}]dec-3(7),9(10)-diene (**81**)	60.35	45.02		24.9
dodecahedrane (**82**)	40.88	67.14		
dodecahedrene (**83**)	85.09	87.48		20.34

[a] Allinger's MM1 force field program[14] was used.

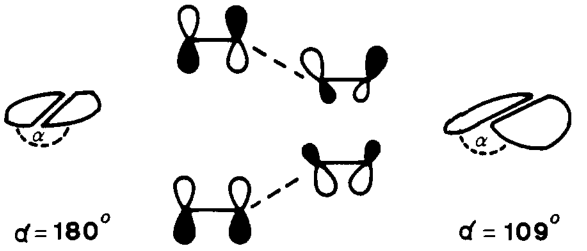
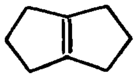


Figure 1. Effect of out-of-plane deformation on an olefin HOMO and LUMO (simplified).

kcal/mol) is a stable olefin, distillable at 118 °C;[43] our OS rules would predict instability at room temperature.

In polycyclic systems, *nonplanar* zero-bridged olefins are possible. The reactivity of the double bonds in such systems is expected to be increased by out-of-plane deformation. As shown in Figure 1, deformation leads to a rehybridization of the two sp^2 carbons toward sp^3. This deformation, described by the dihedral angle α, results in an increase of the energy of the HOMO and lowers that of the LUMO. The rehybridization of the olefinic carbons makes them electronically as well as sterically more favorably disposed toward electrophilic attack. Increased reactivity results. For three-, four-, and five-membered rings, an out-of-plane deformation also reduces the strain energy associated with the σ skeleton.

A series of related olefins, the unbridged parent, bicyclo[3.3.0]oct-1(5)-ene (**74**), and two bridged derivatives, **77** and **79**, illustrate these expectations. The deformation values, α, shown below are derived from force field calculations.

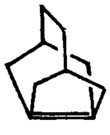


74

$\alpha = 180°$

77

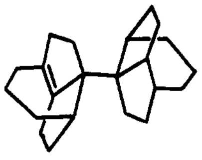
$\alpha = 130°$



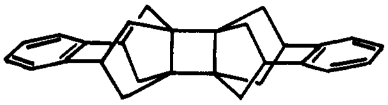
79

$\alpha = 119°$

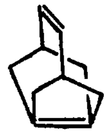
Planar **74** is distillable.[44] The behavior of tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene (**77**) is quite different. The OS value of **77** is 21.1 kcal/mol, almost identical with that of the stable **72**. But when **77** was generated at about 130 °C, only its dimer **88**, formed by an ene reaction, could be isolated.[45] The out-of-plane deformation of rigid **77** leads to this difference. A similar OS value (24.9 kcal/mol) is calculated for diene **81**. When the 9,10-benzo derivative of **81** was generated in refluxing tetraglyme,[46] only the cyclobutane 2 + 2 dimer **89** could be isolated in 40% yield. The out-of-plane angle, α, of 119° in **79** suggests the olefinic carbon to have nearly ideal sp^3 hybridization; ready 2 + 2 dimerization is understandable. This type of dimerization contrasts with that exhibited by **77**. Because of the limited experimental data, no general rules regarding stability can be formulated for zero-bridged olefins. Can, for example, dodecahedrene (**83**) be expected to be isolable? Perhaps not. The calculated OS and α- values are calculated to be similar to those of **77**.



88



89



81

Conclusions and Prospects

The olefinic strain, OS, which can be calculated by empirical force field programs, correlates well with the observed stability of bridgehead olefins. This correlation is not applicable to all types of systems with strained double bonds. In bridgehead olefins, the olefinic strain is largely due to twisting around the double bond; this decreases the HOMO − LUMO difference. Highly twisted bridgehead olefins thus have significant diradicaloid character[47]

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(42) Casanova, J.; Bragini, J.; Cottrell, F. D. *J. Am. Chem. Soc.* **1978**, *100*, 2264. Wiberg, K. B.; Burgmaier, G. J.; Warner, P. *Ibid.* **1971**, *93*, 246. Casanova, J.; Rogers, H. R. *J. Org. Chem.* **1974**, *39*, 3803. Wiberg, K. B.; Bailey, W. F.; Jason, M. E. *Ibid.* **1974**, *39*, 3803.

(43) Kirmse, W.; Pook, K. H. *Angew. Chem.* **1966**, *78*, 603. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 594.

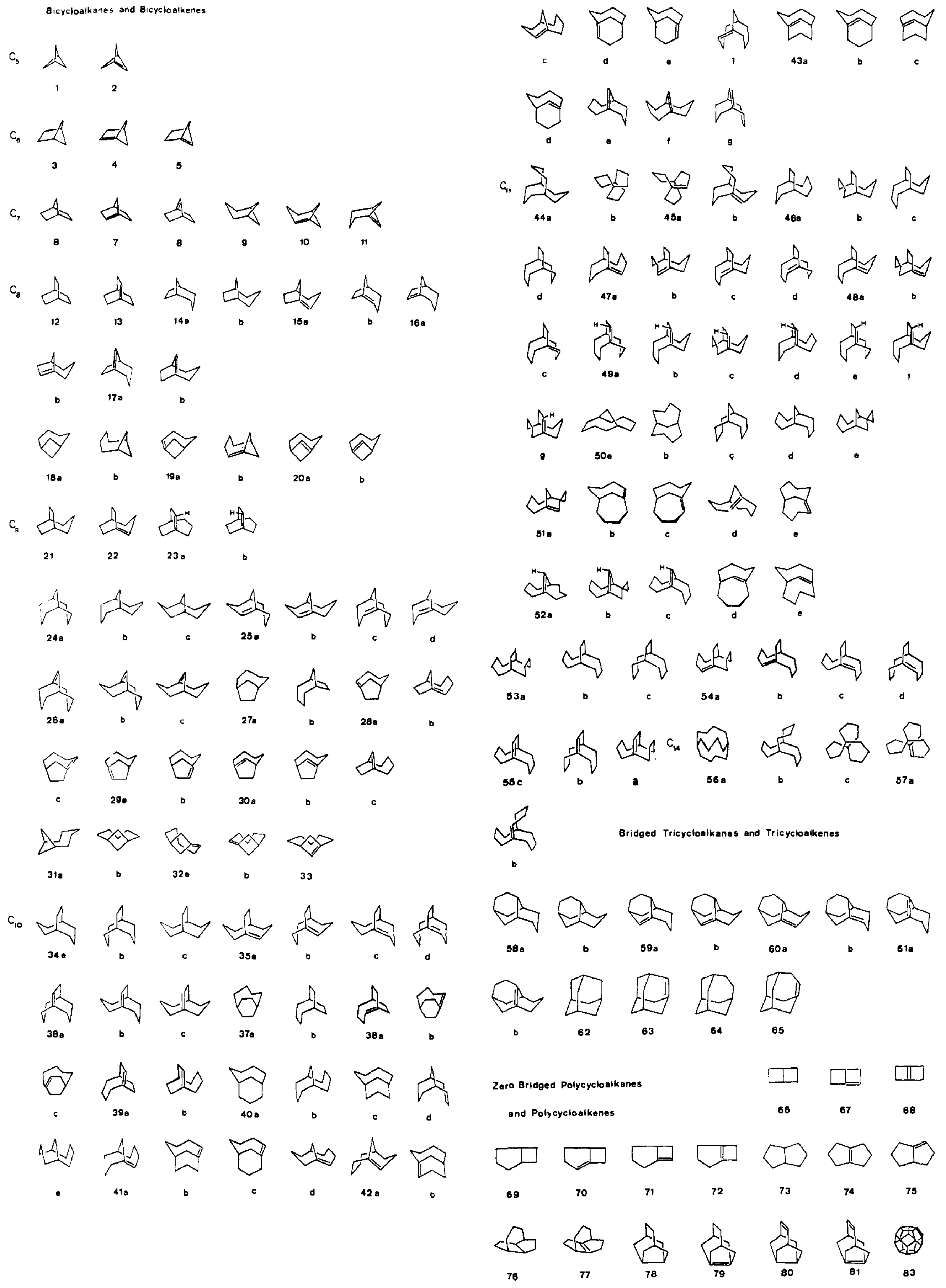
(44) Vogel, E. *Ber. Deutsch. Chem. Ges.* **1952**, *85*, 25.

(45) Greenhouse, R.; Borden, W. T.; Ravindranathan, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 6955.

(46) Greenhouse, R.; Borden, W. T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 1664.

(47) Maier, W. F.; Schleyer, P. v. R.; Crans, D.; Snyder, J. P.; Chandrasekhar, J., unpublished calculations. Maier, W. F.; Schleyer, P. v. R., Paper presented at the IUPAC Conference on Physical Organic Chemistry in Santa Cruz, California, 1980, Abstract C.23, p 77.

Table II. Structures and Conformations Calculated[a]



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[a] The drawings are schematic rather than exact and are meant to represent the general conformations found to be minima on the potential energy surfaces. The exact structures calculated are given in the supplementary material.

Table III. Summary of OS Values (kcal/mol) of Bridged Bicyclic Bridgehead Olefins[a]

S no.	bicyclic system[b]	bridge length where double bond is located				
		1	2	3	4	5
3	111	21.0				
4	211	33.2	25.0			
5	221	38.5	34.9			
	311	39.1		28.9		
6	222		40.4			
	321	36.7	27.2	28.6		
	411	37.8			35.0	
7	322		20.6	19.5		
	331	48.2		15.2		
	421	21.6	9.1		14.1	
	511	14.5				17.5
8	332		18.9	4.7		
	422		7.9		8.2	
	431	22.0		3.0	2.5	
9	333			3.9		
	432		1.4	−7.2	−5.4	
	441	22.3			−1.5	
10	442		5.0		−13.0	
11	444				−14.1	

[a] Ordered according to the *S* number of the system and the length of the bridge in a bicyclo[*x*.*y*.*z*]alkene in which the double bond is located. $S = x + y + z$. [b] Shorthand notation, *xyz*, to designate a bicyclo[*x*.*y*.*z*]alkene.

and enhanced reactivity. In contrast, the stability of zero-bridged olefins is not related directly to their OS values but depends on the degree of out-of-plane deformation imposed by incorporation into rigid cage structures.

Qualitative rules such as those of Köbrich do not predict bridgehead olefin stabilities accurately. Wiseman is correct, all observable bridgehead olefins do have the trans double-bond moiety in an eight numbered or larger ring. However, some systems which meet this criterion are not observable and the relative stability of isomers are not predictable. Quantitative calculations provide the best guide for the experimentalist who wishes to investigate a new system.

The "hyperstable" olefins, which we have examined calculationally, deserve experimental investigation. Such olefins are *stabilized* rather than destabilized because of their location at a bridgehead and should be thermodynamically more stable than any of their positional isomers. Hyperstable olefins should be remarkably unreactive.

Highly strained trisubstituted bridgehead olefins offer an as yet unexplored opportunity for stabilization: replacement of the vinyl hydrogen by bulky groups or substituents which provide electronic stabilization might result in observable species. We are examining such systems both experimentally and calculationally. Of course, our OS generalizations for trisubstituted olefins are not directly applicable to such tetrasubstituted analogs.

It is of interest to recalculate the systems reported in this paper by using new and more accurate empirical force fields. This will be facilitated greatly by the results reported here. Since the minimum energy conformations we have located, often with considerable effort, are not expected to be force field dependent, new calculations need to be carried out only on the most stable conformer (or conformers, where more than one form is competitive in energy) of each system. Coordinates of all conformers we have examined are available as supplementary material to this paper.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by the Deutsche Forschungsgemeinschaft. We thank Dr. J. Chandrasekhar and Professor Maitland Jones for stimulating discussions.

Supplementary Material Available: Tables of the coordinates for all conformers (90 pages). Ordering information is given on any current masthead page.

Tunneling in the Unimolecular Decomposition of Formaldehyde: A More Quantitative Study

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Abstract: Large scale ab initio configuration interaction calculations have been carried out for the reaction path of the unimolecular decomposition of formaldehyde, $H_2CO \rightarrow H_2 + CO$, on its ground-state potential-energy surface. Force constant matrices have also been calculated along the reaction path, making possible a reasonably quantitative treatment of the tunneling dynamics of the reaction within the recently developed reaction path Hamiltonian model. In the energy region of the origin of the $S_0 \rightarrow S_1$ absorption of formaldehyde, the unimolecular decomposition in S_0 is entirely by tunneling, with an average rate at this energy of $\sim 6 \times 10^6\ s^{-1}$.

I. Introduction

The photodissociation of formaldehyde has in recent years assumed the role of a "case study",[1] both experimentally[2-8] and theoretically,[9-17] in the reaction dynamics of small polyatomic molecules. Restricting attention to the collisionless limit of the process, a simplified version of the current picture is that after formaldehyde is excited electronically from its ground electronic

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(1) For example, the recent U.S.-CECAM discussion meeting "Photodissociation of Polyatomic Molecules", Dec 3-4, Veldhoven, Holland, was restricted to the formaldehyde problem.

(2) P. Avouris, W. M. Gelbart, and M. A. El-Sayed, *Chem. Rev.*, **77**, 794 (1977).

(3) A. C. Luntz, *J. Chem. Phys.*, **69**, 3436 (1978).

(4) J. R. Sodeau and E. K. C. Lee, *Chem. Phys. Lett.* **57**, 71 (1978).

(5) H. L. Selzle and E. W. Schlag, *Chem. Phys.*, **43**, 111 (1979).