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1,2-Bridged Cyclopropenes

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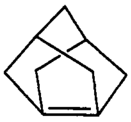
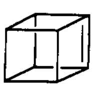
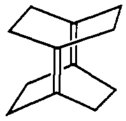
Abstract: The dehalogenations of 1,5-dihalobicyclo[3.1.0]hexanes and 1,6-dihalobicyclo[4.1.0]heptanes have been studied in solution and in the gas phase. The solution reactions led to the formation of bicyclo[3.1.0]hex-1(5)-ene and bicyclo-[4.1.0]hept-1(6)-ene, respectively, but this was followed by rapid ene reactions forming dimers, which then coupled to form tetramers. The cyclopropenes could be trapped as Diels–Alder adducts. In the gas phase, with use of either potassium atoms or solid methyllithium, the products of thermal ring opening, methylenecyclopentene and methylenecyclohexene, were formed. A set of theoretical calculations was carried out dealing with the strain energies, inversion barriers, bond properties, and atom properties of bicyclo[1.1.0]but-1(3)-ene, bicyclo[2.1.0]pent-1(4)-ene, and the cyclopropenes from the experimental study. Whereas bicyclohexene and bicycloheptene appear to be fairly normal compounds except for their high strain energies, bicyclopentene may be a transition state for the carbon scrambling of methylenecyclobutylidene, and bicyclobutene has an unusual structure and charge-density distribution.

Introduction

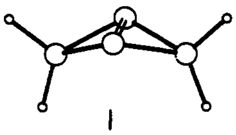
There has been much interest in the effects of bond angle distortion on the structures and properties of alkenes. Pyramidalization may be forced by structural constraints leading to interesting alkenes such as the following:[1,2,3]







We have been interested in other groups of alkenes in which pyramidalization occurs without these constraints.[4] One such group is the 1,2-bridged cyclopropenes, **1–4**.



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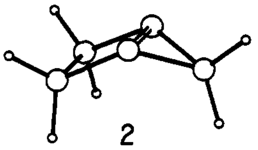

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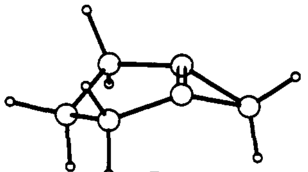

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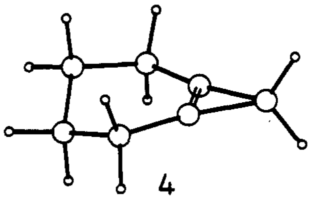

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Table I. Calculated Structures for Cyclopropenes[a]

compd	unit	RHF/6-31G*	MP2/6-31G*
bicyclobutene, planar	C1–C2	1.452	1.469
	C1–C3	1.381	1.476
	C2–H	1.085	1.096
bicyclobutene, bent	C1–C2	1.481	1.487
	C1–C3	1.344	1.409
	C2–H	1.073	1.085 (exo)
		1.084	1.096 (endo)
	α^b	135.1°	138.1°
bicyclopentene, planar	C1–C2	1.528	1.522
	C1–C4	1.295	1.346
	C2–C3	1.573	1.563
	C1–C5	1.488	1.493
	C2–H	1.084	1.095
	C5–H	1.083	1.094
bicyclopentene, bent	C1–C2	1.541	1.538
	C1–C4	1.327	1.382
	C2–C3	1.542	1.537
	C1–C5	1.491	1.498
	C2–H	1.082	1.092 (exo)
		1.084	1.094 (endo)
	C5–H	1.074	1.085 (exo)
		1.085	1.095 (endo)
	α^b	131.7°	128.9°
bicyclohexene, planar	C1–C2	1.501	
	C2–C3	1.579	
	C1–C5	1.272	
	C1–C6	1.500	
bicyclohexene, bent	C1–C2	1.506	
	C2–C3	1.559	
	C1–C5	1.291	
	C1–C6	1.495	
	α^b	153.5°	
bicycloheptene, C_2	C1–C2	1.489	
	C2–C3	1.551	
	C3–C4	1.550	
	C1–C6	1.272	
	C1–C7	1.500	

[a] Bond lengths are given in angstroms, and bond angles are given in degrees. Most of the C–C–C bond angles are given in Figures 1 and 2. [b] The angle between the two rings.

One of the first detailed examinations of these compounds was a theoretical study by Wagner et al.[5] They found that for **1–3** the preferred geometries were nonplanar and that pyramidalization decreased as the size of the bridging ring was increased. We have reported calculations at a somewhat higher theoretical level and confirmed these conclusions.[4] The structure and vibrational frequencies for **1** have been studied in some detail by Hess et al.[6] with inclusion of correction for electron correlation. It was then of interest to try to prepare and study some of these compounds, and this will be a major part of this report. Some additional theoretical calculations also will be reported.

Theoretical Calculations: Structures, Energies, and Vibrational Frequencies

Since our earlier calculations, it has become apparent that correction for electron correlation plays an important role in determining the geometries of highly strained small ring compounds.[6,7] For this reason, it appeared desirable to obtain the

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(1) Renzoni, G. E.; Yin, J.-K.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 7121.

(2) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

(3) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 2194.

(4) Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85.

(5) Wagner, H. U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210. Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.

(6) Hess, B. A., Jr.; Allen, W. D.; Michalska, D.; Schaad, L. J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 1615. Hess, B. A., Jr.; Michelska, D.; Schaad, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 7546. The MP2/6-31G* energies reported herein are slightly lower than in the above work because the carbon 1s electrons were included in the electron correlation.

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Table II. Calculated Energies of Cyclopropenes and Related Compounds

compd	RHF/6-31G* RHF/6-31G*	RHF/6-31G** RHF/6-31G*	MP2/6-31G** RHF/6-31G*	MP2/6-31G* MP2/6-31G*	MP2/6-31G** MP2/6-31G*	MP3/6-31G** MP2/6-31G*
bicyclobutene, planar	−153.55949	−153.56598	−154.14309	−154.11475	−154.14708	−154.15317
bicyclobutene, bent	−153.58020	−153.58686	−154.15663	−154.12699	−154.15948	−154.17182
bicyclopentene, planar	−192.59658	−192.60615	−193.31923	−193.27280	−193.32154	−193.35017
bicyclopentene, bent	−192.62153	−192.63125	−193.34832	−193.30222	−193.35086	−193.37815
bicyclohexene, planar	−231.71671	−231.72925	−232.58525			
bicyclohexene, bent	−231.72314	−231.73573	−232.59644			
bicycloheptene, planar	−270.79159	−270.80719				
cyclopropene	−115.82305	−115.83053	−116.25145	−116.21957	−116.25238	−116.27490
1,2-dimethylcyclopropene	−193.91214	−193.92520	−194.64563	−194.58102	−194.64660	−194.68740
methylenecyclobutylidene	−192.65665	−192.66668	−193.31161	−193.28898	−193.33744	−193.38049
methane	−40.19517	−40.20170	−40.36986	−40.33704	−40.36978	−40.38797
ethane	−79.22876	−79.23823	−79.55368	−79.50397	−79.55361	−79.58292
propane	−118.26365	−118.27616	−118.74078	−118.67441	−118.74074	−118.78058
n-butane	−157.29841	−157.31395	−157.90728			

Table III.

a. Heats of Formation and Relative Energies of Cyclopropenes (kcal/mol)

	ΔH_f			E_{rel}		
compd	RHF 6-31G*	MP2 6-31G*	MP3 6-31G**	RHF 6-31G*	MP2 6-31G*	MP3 6-31G**
bicyclobutene, planar	161	143	154	13.1	7.8	11.7
bicyclobutene, bent	148	135	142	0.0	0.0	0.0
bicyclopentene, planar	156	147	150	15.8	18.4	17.6
bicyclopentene, bent	140	128	133	0.0	0.0	0.0
bicyclohexene, planar	98	94[a]	[96][b]	4.0	7.0	
bicyclohexene, bent	94	86[a]	[90][b]	0.0	0.0	
bicycloheptene, planar	73					
cyclopropene	66					
1,2-dimethylcyclopropene	44					

b. Strain Energies of the More Stable Conformers and Their Olefinic Strain (kcal/mol)

compd	ΔH_f	SE	SE(alkane)[c]	OS	compd	ΔH_f	SE	SE(alkane)[c]	OS
bicyclobutene	142	127	64	63	bicycloheptene	73	73	27	46
bicyclopentene	133	123	55	68	cyclopropene	66	52	28	24
bicyclohexene	90	85	31	54	1,2-dimethylcyclopropene	44	45	25[d]	20

[a] Calculated at HF geometry. [b] Estimated value. [c] Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. [d] Wiberg, K. B.; Lupton, E. C.; Wasserman, D. J.; de Meijere, A.; Kass, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 1740.

Table IV. Calculated Vibrational Frequencies, 6-31G*

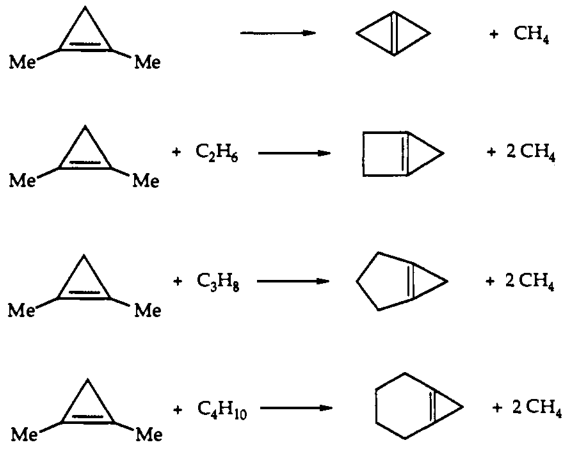
	ν(C=C)		ν(ring opening)[a]	
compd	calcd	obsd	calcd	obsd
cyclopropene	1638	1635	617	596
1,2-dimethylcyclopropene	1895	1885	371	
bicycloheptene	1854		378	
bicyclohexene	1703		315	
bicyclopentene	1530		130*i*	
bicyclobutene	1391		356	

[a] Frequency of normal mode that corresponds to the motion involved in cleavage to a vinylcarbene.

MP2/6-31G* optimized geometries of **1** and **2**, both planar and bent. The RHF/6-31G* and MP2/6-31G* structures are compared in Table I, and the energies are summarized in Table II. It was not practical to carry out MP2 geometry optimizations for **3** and **4**, but here the effect of electron correlation on the structures would be expected to be smaller.

The effect of electron correlation on the structure of **1** was relatively large and in agreement with previous work.[6] In the planar form, the C=C length increased from 1.381 Å to 1.476 Å, and in the bent form the increase was from 1.344 Å to 1.409 Å. Similar changes in C=C lengths were found with the planar and bent forms of **2**, but they were somewhat smaller than for **1**. With the less strained cyclopropene, the increase in C=C bond length was much smaller, changing from 1.276 Å to 1.301 Å.

We have been interested in the heats of formation and strain energies of these compounds. Several approaches are available such as the use of homoisodesmic reactions[8] or group[9] and atom[10] equivalents. Since the latter have not as yet been well-defined for MP2 and MP3 energies, we have chosen to use the former approach and the following hypothetical reactions:



The calculated energies of the cyclopropenes are given in Table II, and the corresponding energies of the acyclic hydrocarbons are available (Table II). From these data, the energy changes

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(7) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247.

(8) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 298 ff. George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

(9) Wiberg, K. B. *J. Comput. Chem.* **1984**, *5*, 197. *J. Org. Chem.* **1985**, *50*, 5285.

(10) Ibrahim, M. R.; Schleyer, P. v. R. *J. Comput. Chem.* **1985**, *6*, 157.

for each of the reactions may be obtained. Assuming that zero-point energies[11] and heat capacities will cancel for these reactions, the energy change may be equated to the heat of reaction. The heats of formation of the *n*-alkanes are known[12] and that of 1,2-dimethylcyclopropene was estimated as 44 kcal/mol on the basis of its 6-31G* energy and the group-equivalent method.[13] These data allow the heats of formation of the cyclopropenes to be estimated.

The energies thus obtained are given in Table III. The addition of polarization functions to the hydrogens had essentially no effect on the relative energies; all of the MP2 relative energies were essentially the same, and so only one set of relative energies are given for each type of calculation. The heats of formation estimated from the MP2/6-31G** energies were somewhat smaller than those obtained from the HF/6-31G** energies, and the MP3 energies are close to the average of the HF and MP2 energies. In the cases where the MP3 energies were not obtained, the final estimated heat of formation was taken as this average. The strain energies for the cyclopropenes were estimated from the calculated heats of formation and are also given in Table III.[14] The strain energies estimated for **3** and **4** were markedly smaller than those for **1** and **2**, but were still significantly larger than that estimated for 1,2-dimethylcyclopropene. The barriers to inversion were calculated to be large for **1** and **2**, drops to ~7 kcal/mol for **3**, and with **4**, the planar geometry for the cyclopropene ring had the lower energy.

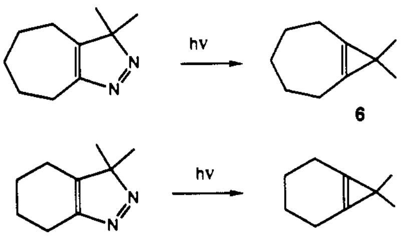
Of more interest than the strain energy is the olefinic strain (OS), which is defined as the difference in strain between the alkene and the corresponding alkane.[15] These energies are given in Table III. The olefinic strain of all the cyclopropenes is large, with 24 kcal/mol for cyclopropene itself. The somewhat smaller value for 1,2-dimethylcyclopropene is in accord with the generally observed stabilization of double bonds by alkyl substituents. A somewhat larger stabilization would be expected here since the olefinic CH bonds of cyclopropenes have a hybridization approaching that of acetylenes.[16] The bridged cyclopropenes are predicted to have markedly increased olefinic strain, with even bicyclo[4.1.0]hept-1(6)-ene having almost twice the olefinic strain of cyclopropene. This must be related to the large C=C—H bond angle of cyclopropene (150°)[17] and the consequent difficulty in bridging the olefinic carbons. It is interesting to note that the olefinic strain energies for **1** and **2** are larger than the rearrangement energies for bicyclo[1.1.0]butane[18] and bicyclo[2.1.0]pentane,[19] respectively. Therefore, one might anticipate difficulties in preparing these alkenes.

The planned syntheses for the bridged cyclopropenes depend on infrared spectroscopy as the analytical tool, and therefore it was important to have a reasonable estimate of the C=C vibrational frequencies. They were calculated at the 6-31G* level, which is known to give good estimates of the observed spectra after scaling by 0.88 to account for the ~1% short bonds calculated without correction for electron correlation and for the effects of anharmonicity in the vibrations.[20] The calculated frequencies are summarized in Table IV. It can be seen that the C=C stretching frequencies for both cyclopropene and 1,2-dimethylcyclopropene are satisfactorily reproduced. The difference in frequency arises from the mass of the methyl carbons that lie close to the C=C axis.[21] Bicycloheptene, **4**, was calculated to have essentially the same C=C vibrational frequency as dimethylcyclopropene. With the smaller bridges, the C=C vibrational frequency decreases considerably.

One interesting observation was that bent bicyclo[2.1.0]pentene had one calculated imaginary frequency, suggesting that it may be a transition state rather than a real molecule. We shall return to this question in a later section of this paper. The vibrational frequencies for the corresponding modes of the other compounds that could lead to ring cleavage also are given in Table IV.

Reactions in Solution

Closs and Böll have reported the preparation of some bridged cyclopropenes via the photolysis of pyrazolines;[22] the alkene, **6** was quite stable and could be heated to 100 °C in solution without change. However, **7** was much less stable and readily underwent rearrangement via a vinylcarbene. Therefore, the reaction does not appear to be useful for the formation of cyclopropenes with four-carbon or smaller bridges. Gassman et al. have presented evidence for the formation of **4** as an intermediate in the reaction of 1-chloro-2-methylcyclohexene with alkyllithiums, but the alkene reacts further under these conditions.[23] Szeimies has presented evidence for the formation of the smaller bridged cyclopropenes, such as **8** and **9**, via elimination of hydrogen halide.[24] However, they only could be identified as Diels–Alder adducts. None of these procedures appeared well-suited to the preparation of compounds such as **3** and **4**.



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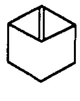

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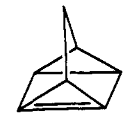

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Dehalogenation of vicinal dihalides has proven to be a useful procedure for the formation of strained alkenes.[1,2,3,20] In order to see if it would be useful in the preparation of cyclopropenes,[25] the dehalogenation of 1,2-dibromo-1,2-dimethylcyclopropane was attempted with *tert*-butyllithium as the reducing agent. The product was isolated as the Diels–Alder adduct with diphenyl-

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[11] Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291.

[12] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986. The heats of formation (kilocalories/mole) are as follows: methane, −17.8; ethane, −20.0; propane, −25.0; and butane, −30.0.

[13] The heat of formation of 1,2-dimethylcyclopropene has been estimated from its heat of hydrogenation to a mixture of 1,2-dimethylcyclopropane, isopentane, and *n*-pentane as 46 kcal/mol: Turner, R. B.; Goebel, P.; Mallon, B. J.; Doering, W. v. E.; Coburn, J. F., Jr.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315.

[14] The energies of the unstrained models were estimated from the Franklin group equivalents: Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070. *J. Chem. Phys.* **1953**, *21*, 2029.

[15] Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

[16] The ^{13}C–^{1}H NMR coupling constant for the vinyl hydrogens is 220 Hz (Closs, G. L. *Proc. Chem. Soc., London* **1962**, 152), which is close to that for acetylenes (250 Hz).

[17] Kasai, P. H.; Meyers, R. J.; Eggers, D. E., Jr.; Wiberg, K. B. *J. Chem. Phys.* **1959**, *30*, 512.

[18] Frey, H. M.; Stevens, I. D. R. *Trans. Faraday Soc.* **1965**, *61*, 90. Srinivasan, R.; Levi, A. A.; Haller, I. *J. Phys. Chem.* **1965**, *69*, 1775.

[19] Chesick, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 3250.

[20] Cf. ref 8, p 226. Wiberg, K. B.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 2184.

[21] Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 73.

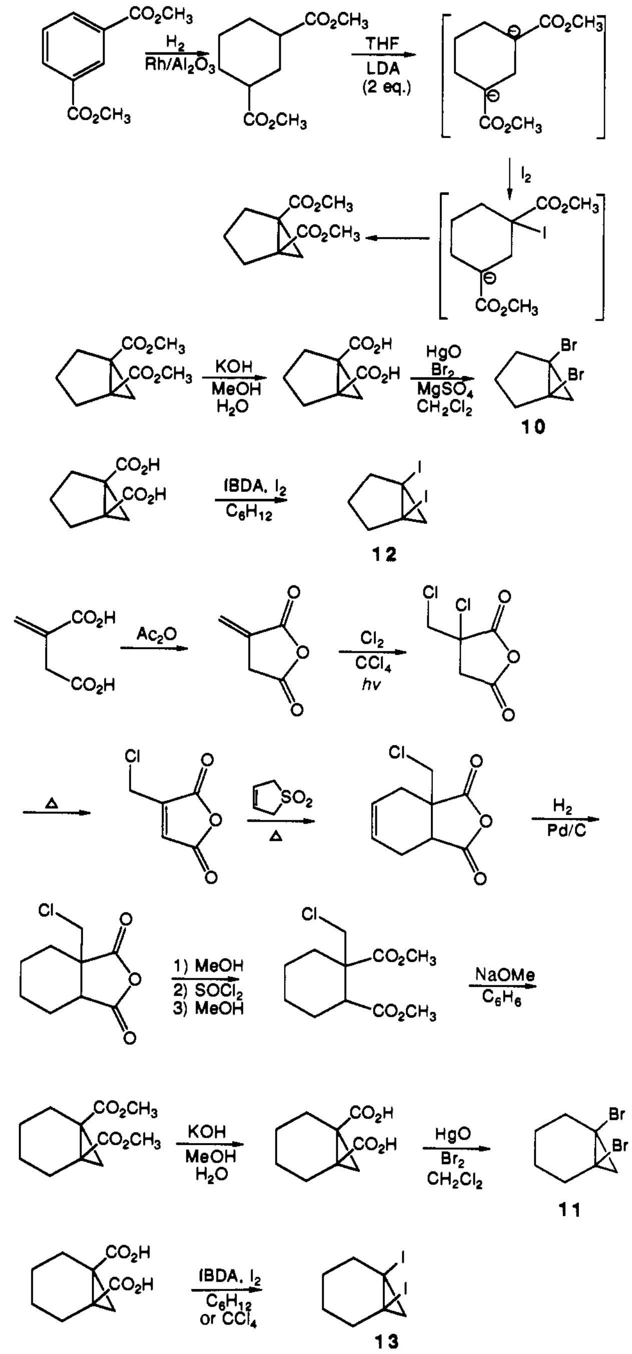
[22] Closs, G.; Böll, W. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 399. Closs, G.; Böll, W. *J. Am. Chem. Soc.* **1963**, *85*, 3094. Closs, G.; Böll, W.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968**, *90*, 173. They reported an infrared C=C bond for **7** at 1740 cm^{-1}, but in view of our calculations (Table III) it seems unlikely that the value is correct.

[23] Gassman, P. G.; Valcho, J. J.; Proehl, G. S. *J. Am. Chem. Soc.* **1979**, *101*, 231. Gassman, P. G.; Valcho, J. J.; Proehl, G. S.; Cooper, C. F. *J. Am. Chem. Soc.* **1980**, *102*, 6519. See: Blanchard, E. P.; Simmons, H. E.; Taylor, J. S. *J. Org. Chem.* **1965**, *30*, 432, for another reaction in which a bridged cyclopropene may be an intermediate.

[24] Szeimies, G. In *Strain and its Implications in Organic Chemistry*; deMeijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989.

[25] A reason to question this reaction is that 1,2-dibromocyclopropane reacts with magnesium to form a bis-Grignard reagent rather than cyclopropene: Wiberg, K. B.; Bartley, W. J. *J. Am. Chem. Soc.* **1960**, *82*, 6375.

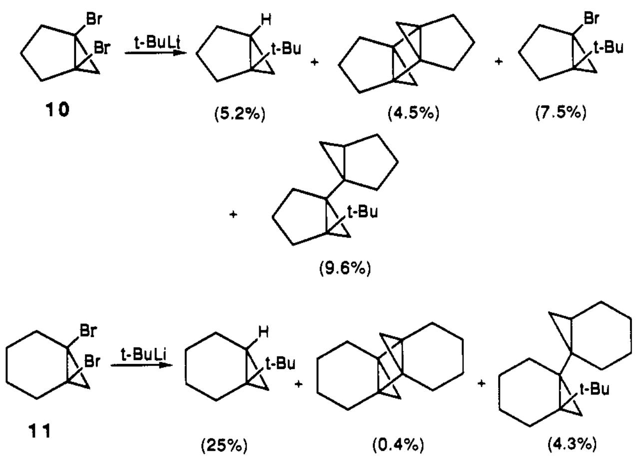
Scheme I

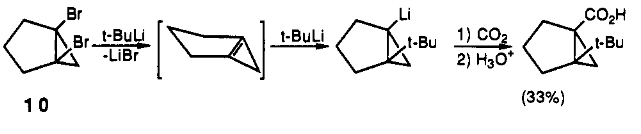


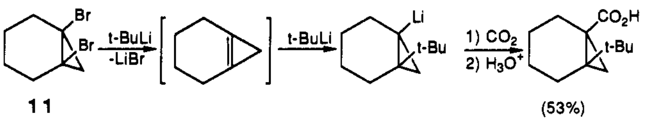
isobenzofuran. The *cis*-dibromide gave a 79% yield of the adduct, and the *trans*-dibromide gave an 83% yield.

The dihalobicycloalkanes needed for the preparation of **3** and **4** were prepared as shown in Scheme I. The dicarboxylic acids could be converted to the dibromides by using the Hunsdiecker reaction with mercuric oxide and bromine[26] and to the diiodides either by using the Hunsdiecker reaction with mercuric oxide and iodine or more satisfactorily by using iodosobenzene diacetate (IBDA) and iodine.[27] The results of the reactions with *tert*-butyllithium are summarized in Scheme II. The reaction of **11** led to the formation of 1-*tert*-butylbicyclo[4.1.0]heptane as the major lower molecular weight product, and the reaction of **10** led to some 1-*tert*-butylbicyclo[3.1.0]hexane. These compounds might reasonably be produced via the initial formation of **3** or **4** followed by the addition of *tert*-butyllithium across the strained double bond. In order to test this hypothesis, the reactions were repeated and the solutions were treated with carbon dioxide before normal workup. In this case, the corresponding carboxylic acids were formed:

Scheme II

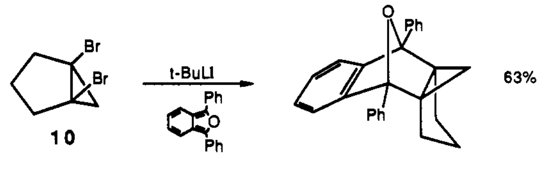


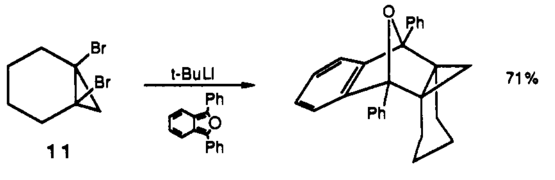




The higher yields of the carboxylic acids suggests that much of the relatively volatile *tert*-butyl-substituted bicycloalkanes were lost in the workup. The reactions with *tert*-butyllithium also led to dimers that could be formed from **3** and **4**, as well as *tert*-butyl-substituted dimers that could be formed via addition of *tert*-butyllithium to another dimer formed via an ene reaction. In addition, higher molecular weight products were found that were originally thought to be polymeric but were later found to be tetramers (see below).

Evidence for the formation of the cyclopropene intermediates was obtained by adding a Diels–Alder trap, 1,3-diphenylisobenzofuran, to the dihalide solutions before adding the *tert*-butyllithium. The corresponding adducts were isolated in good yield. When the diphenylisobenzofuran was added after the *tert*-butyllithium, no adduct was found, indicating the high reactivity of the bridged cyclopropenes. Other Diels–Alder traps were less





effective. With the bicyclo[3.1.0]hexene case, anthracene gave a 4% yield of adduct, furan gave 8%, and 1,4-dimethylfuran gave

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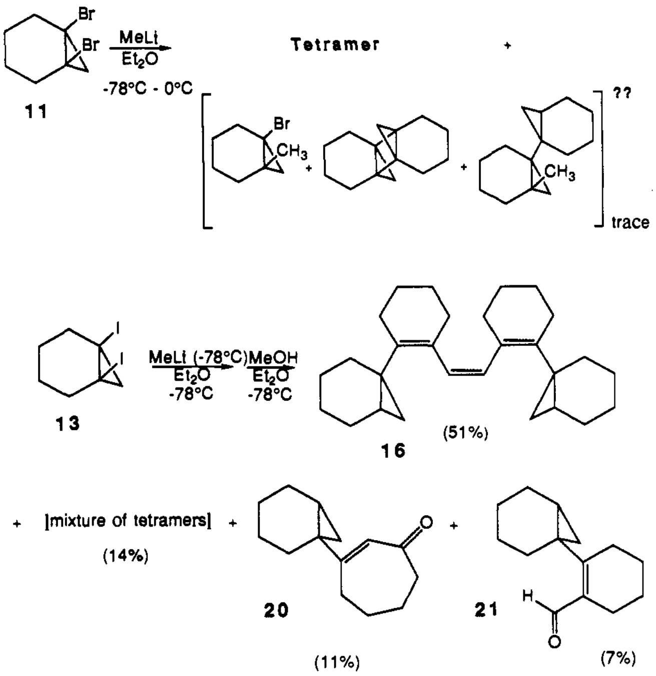
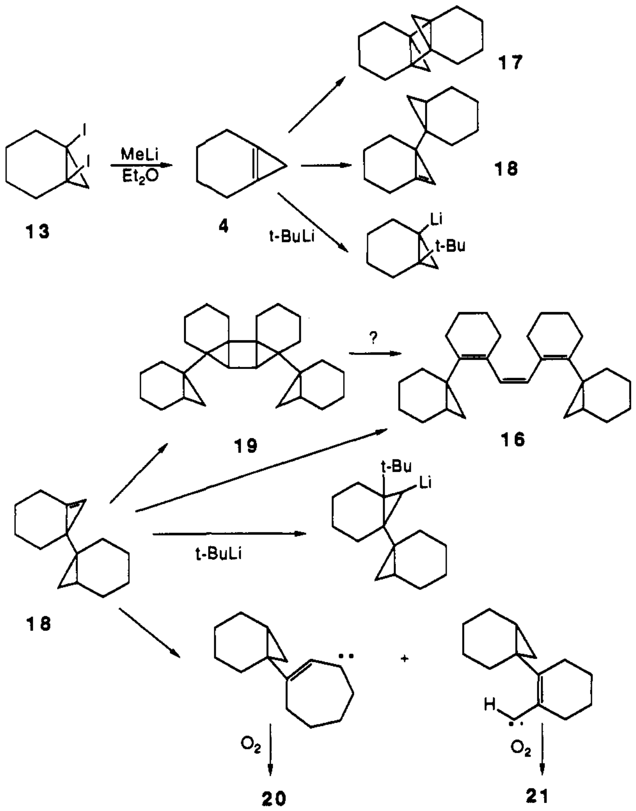
(26) Cristol, S. J.; Firth, W. C. *J. Org. Chem.* **1961**, *26*, 280.

(27) Concepcion, J. E.; Francisco, C. G.; Freire, R.; Hernandez, R.; Salazar, J.; Suarez, F. *J. Org. Chem.* **1986**, *51*, 402.

Scheme III



Scheme IV



7%. Bicyclo[4.1.0]heptene was less reactive and gave no adduct with furan or dimethylfuran.

In order to minimize reaction of the cyclopropenes with the reducing agents, we turned to the use of the less reactive methyllithium. The results of these reactions are summarized in Scheme III. The reaction of the dibromide, **11**, with methyllithium proceeded slowly and gave mainly higher molecular weight products, which proved to be a mixture of tetramers, along with a trace of other products, which were tentatively identified on the basis of the similarity of their NMR spectra and mass spectra to those of the products found in the reaction with *tert*-butyllithium.

The reaction of the diiodide, **13**, proceeded more satisfactorily at a lower temperature and gave a mixture of tetramers along with an unsaturated ketone (**14**) and aldehyde (**15**). The major tetramer was a triene (**16**) whose ^{13}C NMR spectrum showed three double bonds and a plane of symmetry, and whose UV spectrum indicated a conjugated triene. The ^1H NMR spectrum had bands characteristic of a monosubstituted bicyclo[4.1.0]heptane. These data suggest the structure assigned to **16** in Scheme III, with either a cis or trans arrangement at the central C=C bond. A small amount of a mixture of saturated tetramers also was found, which corresponded to the tetramers isolated and identified by Billups and Lee.[28] The two carbonyl compounds were identified as 2-(1-bicyclo[4.1.0]heptyl)cyclohexene-1-carboxaldehyde and 3-(1-bicyclo[4.1.0]heptyl)cyclohept-2-en-1-one on the basis of their NMR spectra.

Evidence for the formation of **4** as a true intermediate in the dehalogenation of **13** was obtained by carrying out the reaction at −105 °C and quenching with methanol at −105 °C followed by the addition of diphenylisobenzofuran. Here, 6% of the Diels–Alder adduct was found along with the expected products from the dimerization of **4**. These conditions eliminate the possibility that the DA adduct was formed by the addition of an initially formed iodo–lithio compound to the diene followed by elimination of lithium iodide.

The course of the reaction of **13** may now be described as shown in Scheme IV. After **4** is formed, it may dimerize in two different fashions forming **17** and **18**. It may also add *tert*-butyllithium but not methyllithium. The initially formed ene product (**18**) might undergo any one of several reactions. Dimerization in the fashion observed with other strained alkenes could give the tetramer **19**. The dimerization would presumably involve a 1,4-diyl intermediate that could undergo cleavage to give the triene **16**,[29] but then the cleavage would have to occur rapidly enough that only one configuration about the central double bond would be formed. Alternatively, **16** might be formed by cleavage of one of the tetramers. The assignment of a cis configuration to the central double bond of **16** corresponds to this mode of formation, but it should be noted that the configuration is not known. The ene dimer may also add *tert*-butyllithium. Cleavage to a vinylcarbene may occur in either one of two ways, forming **20** and **21**. If oxygen were present, they could react to form the two carbonyl compounds that were observed.

Although a general outline of the reactions can be given, there are a number of questions that cannot be answered on the basis of the presently available data. May the carbonyl compounds be formed by reaction of oxygen with **18** without intervention of the vinylcarbenes? What is the stereochemistry of the ene dimer? Two pairs of enantiomers are possible, and if both were formed they could lead to different reactions. What is the stereochemistry of the tetramers formed by dimerization of **19**? There is the possibility of cis and trans isomers as well as syn and anti isomers with respect to the central tricyclohexane framework. Billups and Lee have isolated and determined the structures of two of the tetramers that were formed from a different starting material,[28] and we have observed the same tetramers but formed in small amount. The triene, **16**, may have been formed from one of the other isomeric tetramers, but as noted above it is possible that it is formed from an intermediate diyl. It is also possible that the triene is formed via the vinylcarbene, **21**, but then one would have expected to find both the cis and trans isomers about the central C=C. However, only one was formed.

The reaction of 1,5-diiodobicyclo[3.1.0]hexane with methyllithium led to very different reaction products. They were identified by their spectral data. Two diastereotopic 1-iodo-5-(ethoxyethyl) derivatives were found, and these were formed in

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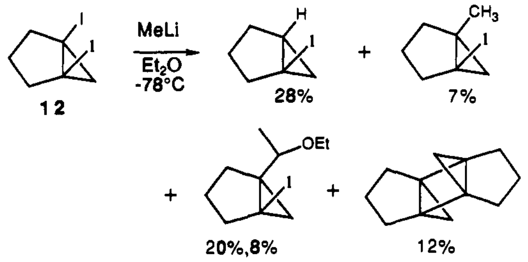
[28] Billups, W. E. Personal communication.

[29] A reaction of this type has been observed by Padwa, A.; Kennedy, G. D.; Newkome, G. R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1983**, *105*, 137.

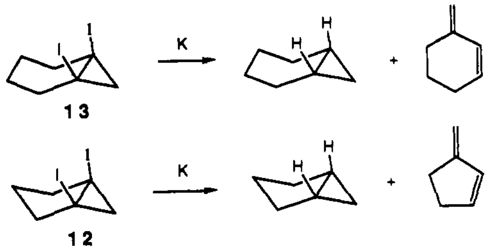
a total of 28% yield. A very small amount of two tetrameric products were found, but the quantitites were too small to be isolated. When the reaction mixture was quenched with carbon dioxide, no carboxylic acids were isolated. Similarly, when the reaction mixture was quenched with methanol-*d*, there was no deuterium incorporation. A reaction carried out at −105 °C gave only monoiodide, indicating that loss of lithium iodide is slow in this case.



The products appear similar to those formed by the reaction of the corresponding dibromide with *tert*-butyllithium. Initial formation of **3** could be followed by methyllithium addition and a metal–halogen interchange with the diiodide to form the methyl-substituted monoiodide. If the initially formed 1-iodo-2-lithiobicyclo[3.1.0]hexane had some lifetime before losing lithium iodide, it could abstract a hydrogen from ether to give the monoiodide. The (ethoxyethyl)lithium thus formed could add to **3** followed by a metal–halogen exchange to give the ethoxyethyl iodides. The results can be rationalized by the considerably increased olefinic strain of **3** over that in **4** (Table IIIb), leading to a less facile formation of the bridged cyclopropene and a higher reactivity toward organolithium compounds.

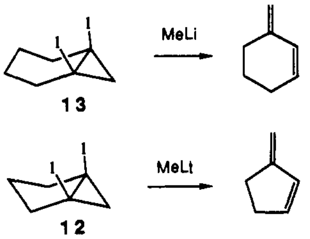
Reactions in the Gas Phase

The major problem with the solution-phase reactions was the rapid ene reaction of the initially formed cyclopropenes. It seemed possible to circumvent the problem by carrying out the dehalogenation in the gas phase and trapping the product as an argon matrix at 20 K. This procedure has been successful in the formation of *o*- and *p*-xylylene[30] and of several small ring propellanes that undergo rapid polymerization when the argon matrix softens at 50 K.[31] The reaction of **13** with potassium atoms in an argon stream was carried out in the same fashion as for the preparation of the propellanes. The infrared spectrum of the argon matrix showed norcarane, the reduction product from **13**, and a small amount of methylenecyclohexene. No bands that could reasonably be attributed to **4** were found. The dibromide, **11**, gave the same products in roughly the same proportion. Complete reduction products are commonly formed in reactions of this type, and norcarane was an expected product. However, it was surprising to find methylenecyclohexene.



The reaction also was carried out with diiodide **12** and dibromide **10**, and here the products were northujane and methylenecyclopentene, formed in a 2:1 ratio. Again, no spectral evidence for the formation of a cyclopropene was found. It is likely that the methylenecycloalkenes were formed from the cyclopropenes via a vinylcarbene intermediate, and it appears that this process is quite facile with these compounds. The thermal rearrangement of cyclopropenes has received considerable study but normally occurs only at elevated temperatures.[32] The facile reactions of the bridged cyclopropenes presumably arise from their high strain energies.

The reaction zone must be heated for these reactions in order to have a useful concentration of potassium atoms in the gas phase. In order to be able to use a lower temperature, we tried the use of methyllithium on glass helices[33] as the dehalogenation reagent, again carrying the dihalide in as an argon stream and collecting the products at 20 K. The temperature of the reaction zone was varied from −15 to 25 °C. The infrared spectrum of the product from **13** or **11** showed only methylenecyclohexene, and the product from **12** or **10** was only methylenecyclopentene. It then appears that even under these milder conditions, the bridged cyclopropenes undergo ring cleavage leading to the rearranged products. During these experiments, a strong exotherm was observed when the apparatus was not externally cooled, and therefore the local temperature at the methyllithium may have been significantly higher than that of the jacket.



It may be noted that the nature and relative amounts of the potassium atom dehalogenation products were independent of the halogen used, suggesting a common type of intermediate in which the halogen plays little or no role. In addition, the amount of ring-opened product increased substantially as the bridging-ring size decreases. If a stepwise ring-opening mechanism involving an intermediate anionic or radical species were operative, one would expect that the increase in methylenecycloalkene would be due to the relief of the greater strain induced by the smaller bridging ring. In fact, the difference in strain energy between bicyclo[3.1.0]hexane and methylenecyclopentane ($\sim$25 kcal/mol)[34] is slightly lower than that between bicyclo[4.1.0]heptane and methylenecyclohexane ($\sim$28 kcal/mol). There is therefore no additional driving force for the ring opening of intermediates derived from **12** over those derived from **13**. One might therefore suggest that the increase in proportion of ring-opened products from the reactions of **10** and **12** may be due to the formation of **3**, which has considerably more strain than its counterpart, **4**.

Additional evidence for the presence of **4** came from the isolation of a small amount of triene **16** from the methyllithium column after the dehalogenation of **13**. It is possible that the ene dimerization of **4** is sufficiently fast at room temperature, and that this product is nonvolatile under the reaction conditions so that the dimer may accumulate and subsequently react to form the tetramer.

It should be noted that Billups and Lee have presented evidence that **4** may be formed via the reaction of 1-(trimethylsiloxy)-6-chlorobicyclo[4.1.0]heptane in a gas stream with solid fluoride ion.[28] It is possible that this reaction is less exothermic than the dehalogenation, and the temperature at the reaction site is considerably lower. However, even here, the compound is quite reactive.

Although we prefer to prepare compounds with substituents, in the present case it appears necessary to place a *gem*-dimethyl

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(30) Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840.

(31) Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638. Walker, F. H.; Wiberg, K. B.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 2056.

(32) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680. See, however, Baird, M. S. *Top. Curr. Chem.* **1988**, *144*, 137, for some examples of reactive cyclopropenes.

(33) Brinker, U. H.; Ritzer, J. *J. Am. Chem. Soc.* **1981**, *103*, 2116. Billups, W. E.; Lin, L.-J. *Tetrahedron* **1986**, *42*, 1575.

(34) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

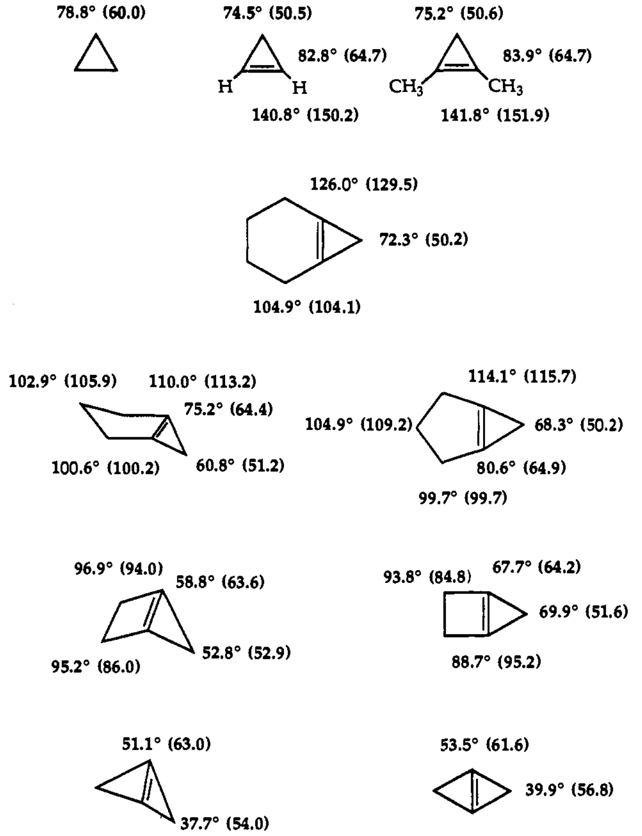

Figure 1. Bond-path angles calculated at the HF/6-31G* level. The bond-path angles are given first followed by the conventional angles in parentheses.

group at the cyclopropene ring in order to prevent the ene reaction. Then, it should be possible to prepare and study the bridged cyclopropenes in solution and determine their infrared and NMR spectra. Studies aimed at preparing the needed precursors are in progress.

Theoretical Calculations: Bond and Atom Properties

Our earlier study of the bond and atom properties of a series of bicycloalkanes proved useful in gaining additional information on the factors that contribute to their strain energies and reactivity.[35] It then appeared desirable to carry out a similar study of the bridged cyclopropenes. We have seen that correction for electron correlation is important in obtaining the structure and energy of these compounds, and therefore the following analysis for **1** and **2** will be carried out with the wave functions derived from both RHF and MP2 calculations at the 6-31G** level, with the corresponding 6-31G* optimized geometries. For a comparison, 1,2-dimethylcyclopropene was studied in a similar fashion. It was not practical to obtain the MP2 optimized geometries for **3** and **4** because of their size, but this should not be so important for these compounds since they have considerably less strain than either **1** or **2**. For these compounds, the analysis was carried out with the RHF/6-31G** wave functions.

The first part of the analysis locates the bond paths and the bond critical points along the paths. The bond path is the path of maximum charge density between a pair of bonded atoms. With cyclopropane derivatives, it is well-known that the bonds are bent, and correspondingly, the angle between the CC bond paths at a cyclopropane carbon are normally considerably larger than the conventional angle. With cyclopropane itself, the bond-path angle is 78° whereas the conventional angle is 60°.

The angles between the bond paths at the carbons are shown in Figure 1. In each case, the bond-path angle is given first, followed by the conventional angle. With 1,2-dimethylcyclopropene and bicyclo[4.1.0]heptene, the bond-path angle at the methylene group is much larger than the conventional angle. However, the difference becomes somewhat smaller with bicyclo[3.1.0]hexene, and with bent bicyclo[2.1.0]pentene, the two angles are the same. With bicyclo[1.1.0]butene, the bond-path angle becomes considerably smaller than the conventional angle. The MP2/6-31G** wave functions give similar results but with a smaller difference between the two types of bond angles (Figure 2). The results indicate that the nature of the bonds in **1** is significantly different than that in **3**, **4**, or 1,2-dimethylcyclopropene. The only known cyclopropane derivative that has a C–C–C bond-path angle smaller than the conventional angle is [1.1.1]propellane. This feature of **1** and of the propellane may indicate an approach to the σ-bridged π type of bonding suggested by Allen and Jackson.[36]

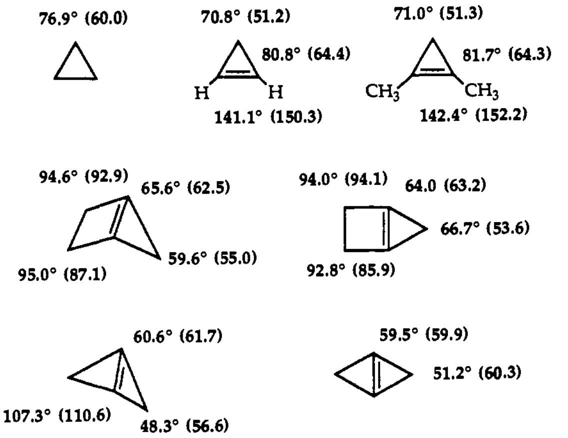

Figure 2. Bond-path angles calculated at the MP2/6-31G* level. The bond-path angles are given first followed by the conventional angles in parentheses.

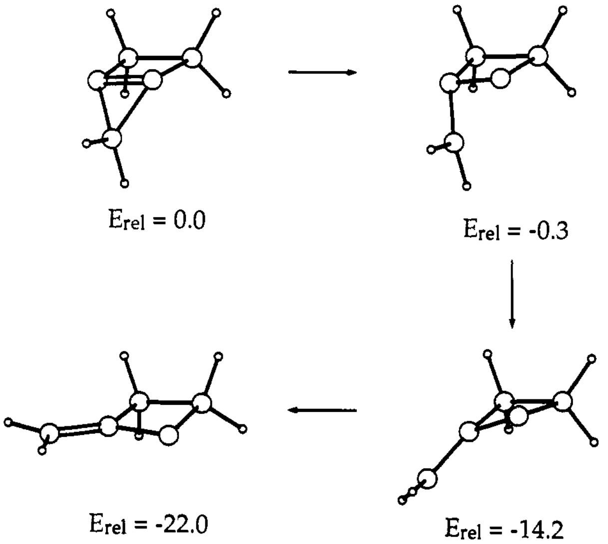

Figure 3. Course of the ring-opening of bicyclo[2.1.0]pent-1(4)-ene calculated at the HF/6-31G* level. The overall reaction is calculated to be considerably less exothermic at the MP3/6-31G* level.

The vibrational frequency calculations also suggested that **2** was different from **3** or **4** in that one imaginary frequency was calculated at the HF/6-31G* level. The course of the reaction was followed at this theoretical level, giving the result shown in Figure 3 with 2-methylenecyclobutylcarbene the final product. At the HF/6-31G* level, the carbene is calculated to be 22.2 kcal/mol more stable than **2**. However, at the MP3/6-31G** level (MP2/6-31G* geometry), the carbene is calculated to be only 1.5 kcal/mol more stable than **2**. Thus, the conclusion about the nature of **2** must be considered as preliminary, and further

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[35] Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985, 1001.

[36] Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591.

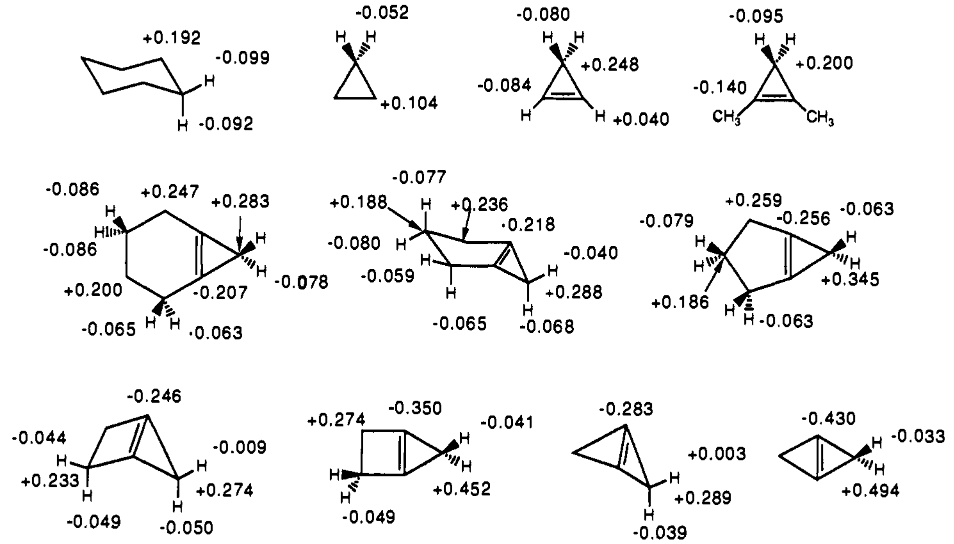

Figure 4. Atomic charges calculated at the HF/6-31G** level.

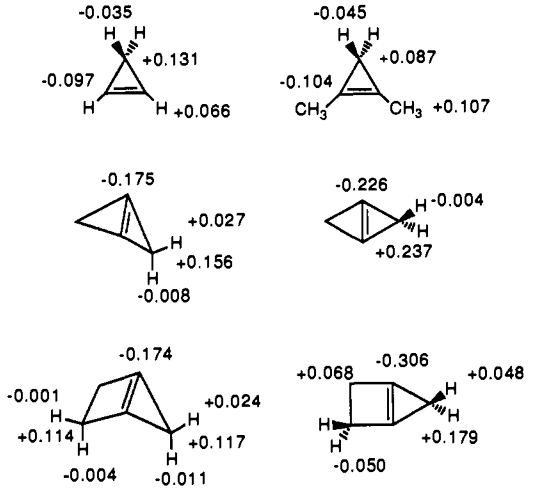

Figure 5. Atomic charges calculated at the MP2/6-31G** level.

work will be done on this system. Nevertheless, it is clear that **2** should undergo ring cleavage more readily than **1**, **3**, or **4**.

Having the bond paths, it is possible to locate the bond critical points that are the points of minimum charge density along the paths. Starting at these points, one may develop a series of rays going away from the bond path for which the charge density decreases most rapidly. A set of such rays will form a surface separating a given pair of atoms, and the set of surfaces (one per bond) will separate the molecule into a series of atomic domains. Integration of the charge density within a given domain will give the electron population for that atom. The populations have been converted to charges by subtracting the nuclear charges and are summarized in Figure 4. In view of the large changes in geometry found with **1** and **2** when correction for electron correlation was included, it might be anticipated that correlation might also have a large effect on the electron populations. They were calculated from the MP2/6-31G* wave functions and are shown in Figure 5 along with data for cyclopropene and 1,2-dimethylcyclopropene.

With unstrained hydrocarbons, the changes in electron populations on going from HF to MP2 wave functions is relatively small.[37] However, with these highly strained compounds, there are rather large changes in populations, only part of which may be accounted for by the changes in geometry on going from HF to MP2. The trends are the same as we have previously noted for other strained compounds.[30] The more strained carbons become increasingly more electronegative and acquire a substantial negative charge in contrast to unstrained carbons, which generally have a small positive charge (cf. cyclohexane and the bridging methylene groups for the bicyclic cyclopropenes). Within the molecular orbital framework, one may regard this increase in electronegativity as coinciding with the increase in the s character of the orbitals from strained atoms to their less strained bonding partners.

The effect of electron correlation is to reduce the polar character of the C–C bonds, and this is generally found to be the case. Even when correlation is included, there are large differences in electron populations at the carbons for the more highly strained compounds.

One may now rationalize the changes that occur in the bridged cyclopropenes as the bridge size is decreased. The increase in bonding between the bridgehead carbons and the adjacent methylenes is matched by a decrease in bonding between the bridgehead atoms. The double bond is thus weakened, and its IR stretching frequency decreases. As the ring size decreases further, one would expect the ability of the lone cyclopropenyl methylene group to provide stabilization to be limited and for the bonds to become more labile. This is observed in the increased propensity of the bridged cyclopropenes to undergo ring-opening reactions to the corresponding methylenecycloalkylidene. Finally, when the larger ring has three or fewer members, the bridgehead atoms become "inverted carbons." The pyramidalization of these olefins is driven by the gain in stability as the bridgehead carbons achieve a more normal geometry. The presence of the nonplanar double bond causes the nature of the solution reactions of these compounds to shift from the facile ene reactions of the less strained cyclopropenes toward [2 + 2] cycloadditions and nucleophilic addition.

Experimental Section

Unless otherwise specified, proton NMR spectra were obtained at 250 MHz in $CDCl_3$ solution, and carbon NMR spectra were obtained at 62.8 MHz in $CDCl_3$ solution. The chemical shifts are reported in ppm downfield from TMS and are based on residual $CHCl_3$ in the solvent. High-resolution mass spectra were obtained on a Kratos MS-80 spectrometer. All reactions were carried out in flame-dried flasks under an inert atmosphere.

Dimethyl Bicyclo[3.1.0]hexane-1,5-dicarboxylate. A solution of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) was prepared from 12.3 mL of diisopropylamine (9.1 g, 90 mmol) in 75 mL of THF and 29.2 mL of butyllithium (2.4 M in hexanes, 70 mmol) at –78 °C. After the solution of LDA was stirred for 15 min, a solution of dimethyl cyclohexane-1,3-dicarboxylate in 55 mL of THF was added dropwise over 30 min. The clear, gold solution was stirred at –78 °C for 1 h, and then warmed to 0 °C over 90 min. The mixture was cooled to –78 °C; a solution of 12.8 g of iodine (48 mmol) in 75 mL of THF was quickly added dropwise with vigorous stirring until reaching the "end point" (when the solution changed from yellow to orange in color) and then was stirred more slowly. The mixture was stirred for 1 h at –78 °C, warmed to 0 °C over 90 min, and finally warmed to room temperature (RT). The

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(37) Wiberg, K. B.; Hadad, C. M.; LePage, T.; Breneman, C. M.; Frisch, M. To be published.

mixture was stirred overnight at RT, poured into a 1-L separatory funnel with 200 mL of 10% aqueous hydrochloric acid, and then extracted with 2 × 200 mL of hexanes. The combined organic layers were washed with 100 mL of aqueous HCl, 200 mL of water, and 2 × 100 mL of 10% aqueous sodium thiosulfate and dried over sodium sulfate. Rotary evaporation of the solvent gave 5.5 g of crude product, which was not further purified. The yield of crude ester was 93%.

Bicyclo[3.1.0]hexane-1,5-dicarboxylic Acid. To the crude diester from the previous step were added 250 mL of MeOH and a solution of 10.0 g of 85% KOH (0.18 mol) in a mixture of 75 mL of MeOH and 25 mL of distilled H_2O. The solution was brought to reflux and allowed to stir overnight. The mixture was cooled to room temperature, and the solvent was concentrated via rotary evaporation. The off-white solid was dissolved in 20 mL of distilled H_2O and extracted with 100 mL of ether. The aqueous layer was acidified to pH 2.0 with 6 N HCl and extracted with ether (4 × 100 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The off-white, crude diacid was recrystallized from ethyl acetate in three crops to give 3.25 g of the white diacid (74%, based on dimethyl cyclohexane-1,3-dicarboxylate): ^1H NMR 10.5–10.3 (br s, 2 H), 2.20–2.42 (m, 2 H), 1.83–2.0 (m, 3 H), 1.65–1.83 (m, 1 H), 1.15–1.43 (m, 2 H); ^{13}C NMR 172.92, 40.77, 27.44, 21.03, 19.26; MS (M^+) calcd 170.0579, found 170.0586.

1,5-Dibromobicyclo[3.1.0]hexane. To a three-necked 50-mL flask equipped with a 25-mL addition funnel, stir bar, condenser, and nitrogen line were added 2.1 g (24.7 mmol) of HgO, 0.7 g (4.12 mmol) of bicyclo[3.1.0]hexane-1,5-dicarboxylic acid, and 30 mL of methylene chloride. The mixture in the flask was brought to reflux and illuminated with a 150-W floodlamp, and a solution of bromine (0.7 mL, 2.18 g, 140 mmol) in 5 mL of methylene chloride was slowly added over 3 h. Evolution of gas was evident after 30 min and continued throughout the addition. The reaction was worked up by filtration through a sintered glass funnel, addition of pentane, refiltration, washing with aqueous sodium bisulfite (2 × 25 mL), drying with magnesium sulfate, and concentration via rotary evaporation to give 1.2 g of crude product colored by bromine. Purification by preparative gas chromatography (5 ft 1.5% OV-101 on 50/60 Anaprep, 110 °C, t_R = 8.1 min) gave 0.38 g (39%) of the dibromide. On a larger scale, it had bp 55–60 °C at 0.1 Torr: ^1H NMR 2.19–2.42 (m, 4 H), 1.56–1.72 (m, 2 H), 1.42 (d, J = 5.70 Hz, 1 H), 1.11–1.32 (m, 1 H); ^{13}C NMR 41.45 (s), 36.57 (t), 26.27 (t), 22.10 (t). Anal. C, H, Br.

1,5-Diiodobicyclo[3.1.0]hexane. A 300-mL three-necked flask was fitted with stoppers, condenser, and nitrogen line and was charged with 0.548 g (3.22 mmol) of bicyclo[3.1.0]hexane-1,5-dicarboxylic acid, 1.14 g (3.55 mmol) of iodosobenzene diacetate (IBDA), 0.9 g (3.55 mmol) of iodine, and 180 mL of cyclohexane. The mixture was illuminated with a 150-W lamp and was brought to reflux. After 1 h, additional portions of IBDA (1.14 g, 3.55 mmol) and iodine (0.9 g, 3.55 mmol) were added. The mixture was heated at reflux for one more hour, cooled to room temperature, and filtered through a medium-frit funnel, yielding the starting diacid (0.24 g, 44%). The solution was washed with 10% aqueous sodium thiosulfate and water, dried over sodium sulfate, and concentrated. The mixture was purified by flash chromatography on silica gel with hexanes to give 0.24 g of the diiodide (37%, based on diacid used). This material could be recrystallized from pentane at −45 °C to give a white solid, mp ~24 °C: ^1H NMR 2.25–2.53 (m, 4 H), 1.59–1.67 (d, 1 H), 1.23–1.39 (m, 2 H), 1.07–1.15 (d, 1 H); ^{13}C NMR 39.60, 29.66, 24.06, 16.45; MS (M^+) calcd 333.8716, found 333.8718.

1-(Chloromethyl)cyclohex-3-ene-1,2-dicarboxylic Anhydride. Into a 500-mL two-necked flask equipped with stir bar, septum, condenser, and nitrogen outlet was placed 1-(chloromethyl)maleic anhydride (67.6 g, 0.46 mol). The compound was degassed by bubbling argon into it for 1 h via a syringe needle through the septum. To the flask was added 3-sulfolene (164.5 g, 1.39 mol), and the mixture was heated at 185 °C. Argon bubbling was continued throughout. The sulfone dissolved and the mixture rapidly darkened to black. Rapid gas evolution was shortly evident. Heating was continued for 15 min after gas evolution ceased, and the product was transferred to a 500-mL flask and Kugelrohr distilled (0.008 Torr, maximum oven temperature 125 °C) to give 56.6 g (63%) of the adduct: ^1H NMR 5.90–6.05 (m, 2 H), 3.93 (d, J = 11.4 Hz, 1 H), 3.63 (d, J = 11.4 Hz, 1 H), 3.51 (d of d, J = 7.35, 2.21 Hz, 1 H), 2.77 (d, 1 H), 2.61 (d of d), 2.26–2.36 (m, 1 H), 2.11–2.18 (m, 1 H); ^{13}C NMR 173.32, 172.95, 124.29, 122.99, 52.01, 51.69, 48.11, 41.07, 28.17, 24.54. Anal. C, H, Cl.

1-(Chloromethyl)cyclohexane-1,2-dicarboxylic Anhydride. Into a Parr hydrogenation bottle were placed 1-(chloromethyl)cyclohex-3-ene-1,2-dicarboxylic anhydride (56.55 g, 0.282 mol), 160 mL of ethyl acetate, and 2.4 g of Pd/C. The mixture was placed on the Parr shaker, purged, and then hydrogenated for 5 h at 20 psi. The reaction appeared to be approximately 50% complete. The catalyst was filtered off and an additional portion of Pd/C was added. The reaction was continued overnight. Hydrogen uptake had then ceased. The mixture was filtered through Celite and concentrated to give 41.8 g (75%) of the anhydride: ^1H NMR 3.98 (d, J = 11.77 Hz, 1 H), 3.68 (d, J = 11.77 Hz, 1 H), 3.53 (m, 1 H), 2.20–2.28 (m, 1 H), 1.55–1.80 (m, 5 H), 1.23–1.46 (m, 2 H); ^{13}C NMR 172.83, 171.31, 50.06, 44.16, 41.34, 30.50, 20.97, 20.05 (2C). Anal. C, H, Cl.

Dimethyl 1-(Chloromethyl)cyclohexane-1,2-dicarboxylate. A 500-mL flask with stir bar, condenser, and argon line was charged with 101.8 g (0.50 mol) of 1-(chloromethyl)cyclohexane-1,2-dicarboxylic anhydride and 300 mL of methanol. The solution was heated to reflux. After 3 h, the excess methanol was removed by rotary evaporation. Thionyl chloride (61.1 mL, 99.7 g, 0.84 mol) was added quickly. The mixture was stirred at room temperature for 15 min and then at 60 °C for 2.5 h. The excess thionyl chloride was removed by rotary evaporation, and the mixture was poured into ice-cooled methanol (150 mL) in a 500-mL flask. The mixture was stirred overnight while slowly warming to room temperature. Concentration gave 116.9 g (94%) of an orange liquid: ^1H NMR 3.70 (s, 3 H), 3.68 (s, 3 H), 2.85–2.92 (m, 1 H), 1.78–2.13 (m, 4 H), 1.36–1.62 (m, 4 H); ^{13}C NMR 173.38, 51.79, 51.53, 49.25, 48.82, 44.43, 29.26, 24.87, 23.08, 21.07.

Bicyclo[4.1.0]heptane-1,6-dicarboxylic Acid. A 1-L flask with stir bar, condenser, nitrogen line, addition funnel, and Dean–Stark trap was charged with 500 mL of anhydrous benzene. Sodium methoxide (33.5 g, 0.62 mol) was added. The addition funnel was charged with dimethyl 1-(chloromethyl)cyclohexane-1,2-dicarboxylate (78.1 g, 0.314 mol) in 30 mL of benzene. This solution was added dropwise over 30 min and the resulting mixture was heated at reflux for 8 h. The reaction mixture was added to 500 mL of distilled water, and the layers were separated. The organic layer was extracted a second time with 500 mL of distilled water, and the combined aqueous layers were extracted once with 100 mL of ether. The combined organic layers were dried over $MgSO_4$ and condensed via rotary evaporation to give 49.8 g (75%) of crude dimethyl bicyclo[4.1.0]heptane-1,6-dicarboxylate: ^1H NMR 3.65 (s, 6 H), 2.29–2.39 (m, 2 H), 1.93 (d, J = 5.15 Hz, 1 H), 1.71–1.81 (m, 2 H), 1.40–1.48 (m, 2 H), 1.23–1.34 (m, 2 H), 0.98 (d, J = 5.15 Hz, 1 H); ^{13}C NMR 172.83, 51.79, 31.41, 25.35, 22.33, 20.00.

The crude ester (132 g, 0.062 mol) was treated with 20.6 g (0.31 mol) of 85% potassium hydroxide in 130 mL of 80% methanol/water. After 30 min of stirring at room temperature, the yellow solution was heated to reflux and stirred overnight. The solution was allowed to cool and was then concentrated to give a yellow solid. This material was dissolved in about 100 mL of water and then acidified to pH 2 to yield an off-white coagulated solid. It was extracted with diethyl ether (6 × 200 mL) and concentrated to give an off-white solid. The solid was recrystallized from diethyl ether/pentane to give 8.05 g (70%) of the acid as an off-white solid. This material could be used without further purification in subsequent steps. Recrystallization from ether/pentane gave the pure diacid, mp 158–160 °C: ^1H NMR 11.45 (br s, 2 H), 2.03–2.46 (m, 2 H), 2.20 (d, J = 4.88 Hz, 1 H), 1.72–1.82 (m, 2 H), 1.26–1.49 (m, 4 H), 1.05 (d, J = 4.88 Hz, 1 H); ^{13}C NMR 179.72, 32.24, 25.14, 23.03, 19.88. Anal. C, H.

1,6-Dibromobicyclo[4.1.0]heptane. To a 250-mL flask equipped with condenser, addition funnel, stir bar, and nitrogen line were added 4.0 g (0.0219 mol) of bicyclo[4.1.0]heptane-1,6-dicarboxylic acid, 5.22 g (0.0434 mol) of magnesium sulfate, 7.96 g (0.0367 mol) of mercury(II) oxide, and 150 mL of methylene chloride. The mixture was brought to reflux. The addition funnel was charged with 2.78 mL (8.67 g, 0.0543 mol) of bromine and 40 mL of methylene chloride. After the reaction mixture had refluxed for 15 min, a slow addition of the bromine/methylene chloride solution was initiated and continued for 75 min. The solution was allowed to stir at reflux for 3.5 h. The mixture was cooled to room temperature and stirred overnight. The mixture was then suction-filtered and concentrated to give a liquid with some white solid suspension. Pentane (50 mL) was added and the suspension was filtered through a sintered glass funnel. The filtrate was concentrated to give 4.6 g (89%) of crude dibromide. If desired, this material could be purified (for use in Displex reactions) by recrystallizing slowly from pentane at −45 °C to give pure white crystals that melted slightly below room temperature: ^1H NMR 2.18–2.59 (m, 4 H), 1.47–1.56 (m, 4 H), 1.44 (d, J = 4.42 Hz, 1 H), 1.21–1.30 (m, 1 H); ^{13}C NMR 39.39, 36.41, 29.80, 21.89. Anal. C, H, Br.

1,6-Diiodobicyclo[4.1.0]heptane. A 500-mL three-necked flask was fitted with a Dean–Stark trap, condenser, stir bar, and stoppers and was charged with 3.05 g (16.58 mmol) of the diacid, 5.87 g (18.23 mmol) of iodosobenzene diacetate, 4.63 g (18.23 mmol) of iodine, and 350 mL of carbon tetrachloride. The reaction mixture was illuminated with a 150-W lamp and brought to reflux. The Dean–Stark trap was emptied frequently at first and then less often after the first 45 min. After 1 h the flask was charged with additional portions of IBDA (18.23 mmol, 5.87 g) and iodine (18.23 mmol, 4.63 g) and was stirred at reflux for 3.5 more hours. The mixture was cooled to room temperature, added to 300 mL of pentane, and washed with 10% aqueous sodium thiosulfate, water, and brine. The combined layers were dried over sodium sulfate and concentrated to give 12 g of a red-brown mixture that was composed of iodobenzene, diiodide, and some anhydride. This mixture was flash chromatographed on silica gel with hexanes to give pure, crystalline diiodide (2.73 g, 47%), mp 48–49 °C: ^{1}H NMR 2.7–2.87 (m, 2 H), 2.45–2.65 (m, 2 H), 1.34–1.51 (m, 2 H), 1.30–1.36 (d, 1 H), 1.10–1.30 (m, 2 H), 1.0–1.1 (d, 1 H); ^{13}C NMR 39.31, 33.71, 22.17, 16.14; MS (M$^+$) calcd 347.8873, found 347.8880.

1,2-Dibromo-1,2-dimethylcyclopropane (Mixture of Cis and Trans). To a 500-mL three-necked flask equipped with a 25-mL addition funnel, condenser, stir bar, and nitrogen line were added 8.7 g (55.1 mmol) of a mixture of *cis*- and *trans*-1,2-dimethylcyclopropanedicarboxylic acid, 20.5 g (94.6 mmol) of mercury(II) oxide, 14.4 g (0.119 mol) of magnesium sulfate, and 400 mL of methylene chloride. The mixture was brought to reflux and stirred for 15 min. The addition funnel was then charged with bromine (6.2 mL, 19.29 g, 0.121 mol) in 15 mL of methylene chloride, and this solution was added, during refluxing, over 30 min. Gas evolution was apparent during the bromine addition. The gas evolution continued for 2.5 h, after which time the mixture was allowed to reflux for an additional hour and then to stir for 4 h at room temperature. The mixture was filtered. The excess salts were washed with pentane. The combined layers were washed with dilute aqueous sodium bisulfite (2 × 15 mL), dried over magnesium sulfate, and concentrated. This crude material was dissolved in 25 mL of pentane and washed with bisulfite (2 × 15 mL). The combined layers were dried over magnesium sulfate and concentrated to give 9.4 g (75%) of the nearly pure dibromide. The isomers could be separated by preparative GC on a 6 ft × $^1/_4$ in. OV-101 column (80 °C). *trans*-Dibromide: ^{1}H NMR 2.07 (s, 6 H), 1.37 (s, 2 H); ^{13}C NMR 40.15, 33.05, 30.94. *cis*-Dibromide: ^{1}H NMR 1.87 (s, 6 H), 1.55 (d, *J* = 7.91 Hz, 1 H), 1.14 (d, *J* = 7.91 Hz, 1 H).

Reaction of 1,2-Dibromo-1,2-dimethylcyclopropane with *tert*-Butyllithium. To a solution of 82 mg (0.36 mmol) of the *cis*-dibromide in 4 mL of dry THF at −78 °C was added 0.3 mL (0.54 mmol) of a 1.9 M solution of *tert*-butyllithium in pentane. After the mixture was stirred at −78 °C for 5 min, 1 mL of methanol was added, followed by a solution of 97.2 mg (0.36 mmol) of 1,3-diphenylisobenzofuran in 1 mL of dry THF. The reaction was allowed to warm to room temperature. Water was added, and the organic layer was taken up in ether. After the solution was dried over MgSO$_4$, the ether was removed, leaving a green oil. It was dissolved in CHCl$_3$ and treated with activated charcoal at reflux. The solvent was removed, and the solid was eluted down a short alumina column with ether to give 95 mg (78%) of the Diels–Alder adduct, mp 149–150 °C: ^{1}H NMR 7.76–7.71 (m, 4 H), 7.46–7.34 (m, 6 H), 7.29–7.24 (m, 2 H), 7.21–7.17 (m, 2 H), 2.25 (d, *J* = 4.82 Hz, 1 H), 1.00 (s, 6 H), 0.80 (d, *J* = 4.89 Hz, 1 H); ^{13}C NMR 149.11, 135.29, 128.84, 128.30 (2C), 125.48, 121.42, 90.21, 32.40, 24.65, 12.62. Anal. C, H.

The reaction was repeated with the *trans*-dibromide (128 mg) giving 157 mg (83%) of the Diels–Alder adduct.

Reaction of 1,5-Dibromobicyclo[3.1.0]hexane with *tert*-Butyllithium. A solution of 201 mg (0.125 mmol) of the dibromide in 12 mL of dry THF was cooled to −78 °C, and 1 mL (1.9 mmol) of a 1.9 M solution of *tert*-butyllithium in pentane was added dropwise over 12 min. After 30 min at −78 °C, 2 mL of methanol was added. The solution was warmed to room temperature, water was added, and the organic layer was taken up in ether. After the solution was dried over MgSO$_4$, the solvent was removed. The product was analyzed by GC on a 5.5 × $^1/_8$ in. 1.5% OV-101 column temperature-programmed at 4 °C/min from 80 °C to 200 °C. Tetradecane was used as an internal standard. Five major products were detected: 1-*tert*-butylbicyclo[3.1.0]hexane (5%); 1-bromo-5-*tert*-butylbicyclo[3.1.0]hexane (8%); pentacyclo-[5.3.1.1.^{2,6}0.0^{2,6}]dodecane (5%); 1-*tert*-butyl-5-(bicyclo[3.1.0]hexyl)bicyclo[3.1.0]hexane (8%); and 1-*tert*-butyl-5-(5-bromobicyclo[3.1.0]-hexyl)bicyclo[3.1.0]hexane (8%). The first three compounds were isolated by GC using a 10 ft 15% OV-101 column at 120 °C.

1-*tert*-Butylbicyclo[3.1.0]hexane: ^{1}H NMR 1.23–1.48 (m, 4 H), 1.28–0.98 (m, 3 H), 0.87 (s, 9 H), 0.49–0.44 (m, 1 H), 0.14 (br t, 1 H); ^{13}C NMR 36.71, 30.72, 28.41, 28.04, 27.93, 21.21, 20.43, 8.64; MS calcd 138.1409, found 138.1402.

1-Bromo-5-*tert*-butylbicyclo[3.1.0]hexane: ^{1}H NMR 2.29–2.21 (m, 2 H), 2.04–1.92 (m, 1 H), 1.61–1.44 (m, 2 H), 1.31–1.10 (m, 2 H), 1.08 (5, 9 H), 1.05–0.93 (m, 1 H); ^{13}C NMR 42.24, 40.20, 39.55, 32.13, 28.99, 27.74, 19.99, 18.15. Anal. C, H, Br.

When the reaction was repeated with 140 mg of the dibromide and 157 mg of 1,3-diphenylisobenzofuran (added before the *tert*-butyllithium), after elution through a short alumina column with ether was obtained 127 mg (63%) of the Diels–Alder adduct, mp 132–133 °C: ^{1}H NMR 7.68–7.64 (m, CH), 7.46–7.37 (m, 6 H), 7.25–7.13 (m, 2 H), 7.10–7.05 (m, 2 H), 2.25 (d, *J* = 5.60 Hz, 1 H), 1.82–1.74 (m, 4 H) 1.33 (d, *J* = 5.60 Hz, 1 H), 1.26–1.18 (m, 2 H); ^{13}C NMR 149.93, 136.91, 128.19 (3C), 125.81, 121.47, 90.75, 44.48, 31.21, 26.28, 18.85. Anal. C, H.

Methyl 1-*tert*-Butylbicyclo[3.1.0]hexane-5-carboxylate. To a solution of 181 mg (0.75 mmol) of 1,5-dibromobicyclo[3.1.0]hexane in 8 mL of dry THF at −78 °C was slowly added 1.2 mL (2.3 mmol) of a 1.9 M solution of *tert*-butyllithium in pentane. After the solution was stirred for 5 min, a large excess of finely crushed dry ice was added. After the mixture was warmed to room temperature, an equal volume of 1 M sodium hydroxide was added. The aqueous layer was washed with ether and then acidified to pH 1 with concentrated HCl. The aqueous layer was extracted four times with ether. The ether solution was dried over MgSO$_4$ and the solvent was removed. The crude acid was treated with ethereal diazomethane prepared from 2 g of *N*-nitroso-*N*-methylurea and 5 g of KOH. Purification via Kugelrohr distillation gave 49 mg (33%) of the ester: ^{1}H NMR 3.67 (s, 3 H), 2.36–2.24 (m, 1 H), 1.98–1.53 (m, 4 H), 1.47 (d, *J* = 5.31 Hz, 1 H), 1.22–0.99 (m, 1 H), 0.92 (s, 9 H), 0.76 (d, *J* = 5.38 Hz, 1 H); ^{13}C NMR 174.62, 51.53, 47.25, 35.16, 32.13, 31.42, 30.34, 28.17, 19.67, 14.14. Anal. C, H.

Reaction of 1,6-Dibromobicyclo[4.1.0]heptane with *tert*-Butyllithium. To a solution of 139 mg (0.55 mmol) of the dibromide in 6 mL of dry THF at −78 °C was added dropwise 0.70 mL (0.83 mmol) of a 1.2 M solution of *tert*-butyllithium in pentane. After 0.5 h at −78 °C, 1 mL of methanol was added and the solution was warmed to room temperature. Water was added and the organic layer was taken up in ether. The ether solution was dried over MgSO$_4$, and the solvent was removed. The product was analyzed by GC on a 5 ft × $^1/_8$ in. 1.5% OV-101 column temperature-programmed at 4 °/min from 80 to 200 °C. Dodecane was used as an internal standard. The major products were the following: 1-*tert*-butylbicyclo[4.1.0]heptane (25%); pentacyclo[6.4.1.1.^{2,7}0.0^{2,7}]tetradecane (0.4%); and 1-*tert*-butyl-6-(bicyclo[4.1.0]heptyl)bicyclo-[4.1.0]heptane (one isomer 1%, second isomer 3%). The products could be isolated by preparative GC on a 5 ft × $^1/_4$ in. 15% OV-101 column at 150 °C.

1-*tert*-Butylbicyclo[4.1.0]heptane: ^{1}H NMR 1.89–1.75 (m, 2 H), 1.69–1.65 (m, 1 H), 1.49–1.42 (m, 1 H), 1.24–1.10 (m, 5 H), 1.00–0.85 (m, 1 H), 0.81 (s, 9 H), 0.60–0.55 (m, 1 H), 0.00 (t, *J* = 5.4 Hz, 1 H); ^{13}C NMR 32.97 (s), 26.69 (t), 26.50 (g), 26.50 (s), 24.15 (t), 22.74 (t), 21.37 (t), 13.94 (d), 13.65 (t). Anal. C, H.

Pentacyclo[6.4.1.1.^{2,7}0.0^{2,7}]tetradecane: ^{1}H NMR 1.70 (br t, *J* = 6.1 Hz, 8 H), 1.29 (d, *J* = 4.41 Hz, 2 H), 1.10–0.98 (m, 8 H), 0.54 (d, *J* = 4.41 Hz, 2 H); MS calcd 188.1565, found 188.1566.

1-*tert*-Butyl-6-(bicyclo[4.1.0]heptyl)bicyclo[4.1.0]heptane. First isomer: ^{1}H NMR 2.07–1.00 (m, 16 H), 0.97 (s), 0.94 (s, 9 H), 0.86–0.02 (m, 4 H), 0.10 (t, 1 H); MS, p at 246. Second isomer: ^{1}H NMR 2.18–1.02 (m), 1.00 (s), 0.97 (s), 0.73–0.56 (m), 0.38–0.16 (m); MS, p at 246.

The reaction was repeated with 158 mg of the dibromide and 170 mg of 1,3-diphenylisobenzofuran (added before the *tert*-butyllithium). The product was recrystallized from pentane to give 160 mg (71%) of the Diels–Alder adduct, mp 145–146 °C: ^{1}H NMR 7.72–7.67 (m, 4 H), 7.46–7.35 (m, 6 H), 7.19 (s, 4 H), 2.21 (d, *J* = 4.94 Hz, 1 H), 1.91–1.81 (m, 2 H), 1.63–1.58 (m, 2 H), 1.04–0.88 (m, 2 H), 1.00 (d, *J* = 4.97 Hz, 1 H), 0.46–0.36 (m, 2 H); ^{13}C NMR 149.81, 135.56, 129.22, 128.46, 128.35, 125.70, 121.37, 91.08, 31.48, 24.00, 22.49, 20.97. Anal. C, H.

Methyl 1-*tert*-Butylbicyclo[4.1.0]heptane-6-carboxylate. To a solution of 143 mg (0.56 mmol) of 1,6-dibromobicyclo[4.1.0]heptane in 3 mL of dry THF at −78 °C was added 0.88 mL (1.68 mmol) of a 1.9 M solution of *tert*-butyllithium in pentane. After 5 min, an excess of finely crushed dry ice was added. The mixture was warmed to room temperature and treated with an equal volume of 1 M NaOH. The aqueous layer was extracted with ether, acidified to pH 1, and extracted with ether. The solution was dried over MgSO$_4$, the solvent was removed, and the product was treated with ethereal diazomethane. The product was distilled in a Kugelrohr apparatus, giving 63 mg (53%) of the ester: ^{1}H NMR 3.57 (s, 3 H), 2.03–1.90 (m, 2 H), 1.76–1.67 (m, 1 H), 1.40–0.90 (m, 8 H), 1.23 (d, *J* = 5.49 Hz, 1 H), 0.79 (s, 9 H), 0.35 (d, *J* = 5.44 Hz, 1 H); ^{13}C NMR 176.35, 51.63, 34.57, 34.24, 31.26, 29.09, 27.68, 26.93, 22.16, 20.53, 16.47. Anal. C, H.

Reaction of 1,6-Diiodobicyclo[4.1.0]heptane with Methyllithium. To a stirring solution of 1.4 g (4.0 mmol) of the diiodide in 500 mL of dry ether at −78 °C was added dropwise 3.9 mL (4.3 mmol) of 1.1 M methyllithium in ether. After stirring for 5 h at −78 °C, a solution of 6 mL of methanol in 50 mL of dry ether was added. The solution was allowed to warm to room temperature overnight and was then added to 250 mL of water. The organic layer was separated, dried over Na$_2$SO$_4$, and concentrated. An NMR spectrum was obtained for the crude mixture. One portion of the products was separated by preparative GC on a 2.5-ft

5% OV-101 50/60 Anaprep column at 165 °C. Three groups of products were collected. The first contained a group of dimeric products (7–10 min), and the second (7–30 min) and third (33–57 min) were two separate tetrameric products. The latter was isolated as 36.3 mg (51%) of a light yellow oil, and found by NMR analysis to be the major product in the crude mixture. The first tetramer was found to be a mixture (10.2 mg, 14%).

A second portion of the crude mixture was attached to a vacuum line, and all the volatile materials were transferred. The resulting mixture was separated by preparative GC on a 2.5-ft 5% OV-101 column at 110 °C, giving two products in 5.6-mg (7%, 10 min) and 8.7-mg (11%, 12 min) yields. They were identified as 2-(1-bicyclo[4.1.0]heptyl)cyclohexene-1-carboxaldehyde and 3-(1-bicyclo[4.1.0]heptyl)cyclohept-2-en-1-one.

Triene **16**: ^{1}H NMR 6.62 (s, 2 H), 2.15–2.3 (br s, 4 H), 2.05–2.15 (br s, 4 H), 1.90–2.05 (m, 4 H), 1.75–1.90 (m, 4 H), 1.45–1.75 (m, 4 H), 1.1–1.45 (m, 8 H), 0.9–1.1 (m, 2 H), 0.35–05 (m, 2 H); ^{13}C NMR (143.08 (s), 129.58 (s), 124.90 (d), 30.27 (t), 29.03 (t), 26.25 (s), 25.65 (t), 23.98 (t), 23.60 (t), 23.40 (t), 23.07 (t), 22.07 (t), 21.22 (t), 19.42 (d); MS (M$^+$) calcd 376.3132, found 376.3131; UV (hexane) λ_{max} 292.5 nm, ϵ = 26 400.

3-(1-Bicyclo[4.1.0]heptyl)cyclohept-2-en-1-one: ^{1}H NMR 5.9 (s, 1 H), 3.4–3.6 (m, 4 H), 1.5–2.0 (m, 4 H), 1.7–1.8 (m, 4 H), 1.15–1.4 (m, 4 H), 1.0–1.15 (m, 1 H), 0.78–0.85 (d of d, 1 H), 0.43–0.5 (d of d, 1 H); ^{13}C NMR 128.24, 105.23, 42.02, 30.80, 29.06, 28.54, 25.71, 23.57, 21.80, 21.25, 21.90, 18.51, 17.42; MS (M$^+$) calcd 204.1515, found 204.1527.

2-(1-Bicyclo[4.1.0]heptyl)cyclohexene-1-carboxaldehyde: ^{1}H NMR 10.38 (s, 1 H), 2.25–2.35 (m, 2 H), 2.10–2.20 (m, 2 H), 1.68–2.05 (m, 4 H), 1.5–1.65 (m, 4 H), 1.15–1.4 (m, 4 H), 1.0–1.15 (m, 1 H), 0.75–0.84 (d of d, 1 H), 0.57–0.65 (d of d, 1 H); ^{13}C NMR 192.95, 100.91, 92.41, 31.42, 29.97, 29.75, 23.07, 22.57, 22.19, 21.83, 21.72, 20.62, 18.56, 18.49; MS (M$^+$) calcd 204.1515, found 204.1523.

The reaction was repeated with 42.7 mg of the diiodide in 50 mL of dry ether at −105 °C and 0.2 mL of precooled 1.38 M methyllithium in ether. After the mixture was stirred for 5 h at −105 °C, a solution of 0.5 mL of dry methanol in 2 mL of dry ether, precooled to −105 °C, was added and the solution was stirred for 5 min. Then, a suspension of 30.8 mg of 1,3-diphenylisobenzofuran in 20 mL of dry ether, precooled to −105 °C, was added. The reaction mixture was slowly warmed to room temperature overnight. The products were separated by flash chromatography on silica gel with first hexane and then 2:1 chloroform/hexane to isolate the unreacted diiodide (81%), followed by 1.4 mg (5%) of the Diels–Alder adduct.

Reaction of 1,5-Diiodobicyclo[3.1.0]hexane with Methyllithium. To a solution of 300 mg (0.9 mmol) of the diiodide in 400 mL of dry ether at −78 °C was added 1.16 mL (1.47 mmol) of 1.29 M methyllithium in ether. It was stirred at −78 °C for 7.5 h, and then 5 mL of dry methanol in 20 mL of dry ether was added. The mixture was allowed to warm to room temperature overnight and was then added to 200 mL of water. The organic layer was separated, dried over Na$_2$SO$_4$, and concentrated. The more volatile products were transferred by bulb-to-bulb distillation on a vacuum line and separated by preparative GC on a 5-ft 20% SE30 column at 110 °C. 1-Iodobicyclo[3.1.0]hexane (28%, 2.5 min), 1-iodo-5-methylbicyclo[3.1.0]hexane (7%, 3.1 min), pentacyclo[5.3.1.1.^{2,6}0.0^{2,6}]dodecane (12%, 11.6 min), and 1-iodo-5-(1-ethoxyethyl)bicyclo[3.1.0]hexane, first isomer (20%, 14.4 min) and second isomer (8%, 16.9 min) were obtained.

1-Iodobicyclo[3.1.0]hexane: ^{1}H NMR 2.05–2.35 (m, 2 H), 1.85–2.05 (m, 1 H), 1.5–1.73 (m, 2 H), 1.3–1.5 (m, 2 H), 1.08–1.3 (m, 1 H), 0.83–1.0 (m, 1 H); ^{13}C NMR 41.12, 28.69, 26.45, 22.009, 18.20, 3.64; MS (M$^+$) calcd 207.9750, found 207.9768.

1-Iodo-5-methylbicyclo[3.1.0]hexane: ^{1}H NMR 2.2–2.4 (m, 2 H), 1.6–1.7 (m, 2 H), 1.2–1.4 (m, 2 H), 1.29 (s, 3 H), 1.11–1.19 (d, 1 H), 0.66–0.72 (d, 1 H); MS (M$^+$) calcd 221.9906, found 221.9913.

1-Iodo-5-(1-ethoxyethyl)bicyclo[3.1.0]hexane. First isomer: ^{1}H NMR 3.48–3.63 (m, 2 H), 3.21–3.29 (g, 1 H), 2.27–2.33 (m, 2 H), 1.83–1.96 (m, 1 H), 1.46–1.59 (m, 3 H), 1.24–1.27 (d, 3 H), 1.19–1.23 (t, 3 H), 1.10–1.12 (d, 1 H), 0.53–0.57 (d, 1 H); ^{13}C NMR 78.53, 64.27, 41.33, 37.18, 23.09, 21.71, 21.11, 19.10, 17.31, 15.89; MS (M$^+$) calcd 280.0325, found 280.0332. Second isomer: ^{1}H NMR 3.54–3.67 (m, 1 H), 3.38–3.50 (m, 1 H), 3.18–3.26 (g, 1 H), 2.15–2.33 (m, 2 H), 1.82–1.95 (m, 1 H), 1.43–1.57 (m, 3 H), 1.32–1.37 (d, 1 H), 1.28–1.32 (d, 3 H), 1.15–1.20 (t, 3 H), 0.95–1.05 (d, 1 H); MS (M$^+$) calcd 280.0325, found 280.0306.

Reaction of Dihalides with Potassium in the Gas Phase. The apparatus was that previously used to prepared [2.2.1] and [2.1.1] propellanes.[38] It consisted of a reaction chamber heated to 125 °C, which was connected at one end to a tube containing potassium that could be heated to ~180 °C, a stopcock with a flask containing the dihalide, and attached at the other end to a port on a Displex unit facing a CsI window, which could be cooled to ~20 K. After the apparatus had been pumped down, the CsI window was cooled and the potassium was heated until it began to sublime. The dihalide was cooled to −78 °C and an argon stream was passed over it and into the reaction chamber. The temperature of the bath cooling the dihalide was raised until it began to sublime slowly. The reaction was allowed to proceed for several hours, during which time ~40–50 mg of the dihalide had been sublimed. The sample flow was stopped and the potassium was cooled. The CsI window was rotated 90°, the apparatus was lowered into the beam of an FT-IR spectrometer, and the infrared spectrum was taken. Helium cooling was stopped, and the window was allowed to warm to room temperature, collecting the products in a liquid nitrogen cooled trap. Some CDCl$_3$ was added and the NMR spectrum was taken.

The reaction of 1,5-dibromobicyclo[3.1.0]hexane was carried out as described above. All of the dibromide had been consumed, and the IR spectrum of the products indicated only 3-methylenecyclopentene and bicyclo[3.1.0]hexane. No bands that could be attributed to bicyclo[3.1.0]hex-1(5)-ene were found. The NMR spectrum of the product indicated that the above products were formed in a 1:2 ratio. Reduction products are commonly found in reactions of this type.[39] The diiodide was studied in the same fashion, giving the same products in essentially the same ratio.

The reaction of 1,6-diiodobicyclo[4.1.0]hexane was carried out as described above. The IR spectrum indicated that all of the diiodide had been consumed and that the major product was norcarane. A small amount of 3-methylenecyclohexene also was observed.

Reaction of Dihalides with Methyllithium in the Gas Phase. The apparatus described above was used, but the tube containing potassium was eliminated. To the reaction chamber was attached a jacket that could be used to control its temperature. The chamber was packed with methyllithium on glass helices (pyrophoric!). After the system had been pumped down and the CsI window had been cooled to ~20 K, the dihalide was introduced in an argon stream. The infrared spectrum of the products was obtained as described above.

The reaction of 1,2-dibromo-1,2-dimethylcyclopropane was carried out with jacket temperature from 70–130 °C and in each case gave ~35% conversion to 1,2-dimethylcyclopropene. The only other product was methyl bromide.

The reaction of 1,6-dibromobicyclo[4.1.0]heptane was carried out with a jacket temperature of 80 °C. The IR spectrum indicated some starting material, 3-methylenecyclohexene as the major product, along with some methyl bromide. The reaction of the corresponding diiodide was carried out under the same conditions, leading to complete consumption of the diiodide. The only products were 3-methylenecyclohexene and methyl iodide. The temperature of the reaction chamber was lowered to −12 °C and the reaction was repeated, giving essentially the same result. At −25 °C, relatively little conversion was obtained, but again the same products were formed.

The reaction of 1,5-diiodobicyclo[3.1.0]hexane was carried out in the same fashion. With a jacket temperature of −5 to −15 °C, the IR spectrum showed some unreacted diiodide, 3-methylenecyclopentene, and methyl iodide. With a jacket temperature of −25 °C, very little reaction occurred.

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