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Ring Opening of Bicyclo[*n*.1.0]alkanones to 2-Cycloalkanone-1,3-diyls. Why Does Oxyallyl Diradical Formation Require Less Energy from Bicyclo[3.1.0]hexan-6-ones than from Bicyclo[1.1.0]butan-2-ones?

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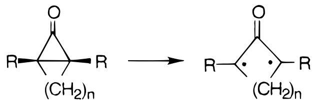
Abstract: CASSCF and CASPT2N/6-31G* calculations have been performed on the opening of bicyclo[*n*.1.0]-alkanones, $n = 1-3$ (**1**−**3**), to the corresponding 2-cycloalkanone-1,3-diyls (**4**−**6**). In agreement with the failure to observe 1,4-dimethylbicyclo[2.1.0]pentan-5-one (**2b**) experimentally, ring-opened 2-cyclopentanone-1,3-diyl diradicals (**5**) are calculated to be lower in energy than the corresponding bicyclo[2.1.0]pentan-5-ones (**2**). Also, in agreement with kinetic experiments on di-*tert*-butyl derivatives **1c** and **3c**, bicyclo[3.1.0]hexan-6-ones (**3**) are calculated to undergo ring opening more easily than bicyclo[1.1.0]butan-2-ones (**1**). This result is surprising since bicyclo[1.1.0]-butane (**7a**) is both calculated and found to have a higher strain energy than bicyclo[3.1.0]hexane (**9a**). Isodesmic reactions are used to show that the comparative reluctance of bicyclo[1.1.0]butan-2-ones (**1**) to undergo ring opening to 2-cyclobutanone-1,3-diyls (**4**) is primarily due to the stabilization of **1** by a strong interaction between the bent bond between the bridgehead carbons, C-1 and C-3, and the carbonyl group at C-2. *Ab initio* calculations of the energies of isodesmic reactions are also used to show that methyl substituents provide considerable stabilization for oxyallyl diradicals **4b**−**6b**, and DFT calculations reveal that steric interactions between the *tert*-butyl groups in **3c** play a minor role in reducing the energy required for its ring opening to **6c**, relative to that required for opening of **1c** to **4c**.

A new synthetic method[1] has allowed 1,*n*+2-dialkylbicyclo[*n*.1.0]alkanones with $n = 1-3$ (**1**−**3**) to be generated at low temperatures and their ring opening to the corresponding 2-cycloalkanone-1,3-diyls[2] (**4**−**6**) to be studied by NMR. For example, assuming that **4c** is the transition state for ring inversion of **1c**, $\Delta G = 16.7$ kcal/mol was obtained for the free energy and $\Delta H = 16 \pm 1$ kcal/mol for the enthalpy difference between the bicyclobutanone and the corresponding 2-cyclobutanone-1,3-diyl.[3]



1, n = 1
2, n = 2
3, n = 3
a, R = H
b, R = CH_3
c, R = $(CH_3)_3C$

4, n = 1
5, n = 2
6, n = 3
a, R = H
b, R = CH_3
c, R = $(CH_3)_3C$

In sharp contrast to the experimental results for **1c**, **2b** could not be detected by NMR, even at −120 °C, under conditions where oxallyl **5b** could be trapped chemically.[4] This finding is consistent with the results of *ab initio* calculations, which predict 2-cyclopentanone-1,3-diyl (**5a**) is more stable than bicyclo[2.1.0]pentan-5-one (**2a**).[5,6]

Like **1c**, bicyclic ketone **3c** is isolable;[7] and NMR studies of the barrier to ring inversion in **3c** give $\Delta G^{\ddagger} = 11.5$ kcal/mol.[8] This is a surprising result, since it indicates a significantly smaller energy difference between **3c** and **6c** than between **1c** and **4c**. One might have predicted just the opposite, since more strain relief would be expected on cleaving the bond between the bridgehead carbons in the bicyclo[1.1.0]butane ring system than in the bicyclo[3.1.0]hexane ring system.[9]

In order to understand this result we have performed *ab initio* calculations of the energy difference between bicyclo[*n*.1.0]-alkanones (**1**−**3**) and the isomeric 2-cycloalkanone-1,3-diyls (**4**−**6**) for $n = 1-3$. We have also investigated the effects of the carbonyl groups in **1**−**3** on the energies required for ring opening, as well as the effects of alkyl substituents at the bridgehead carbons. Herein we report the results of our calculations.

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(1) Black, C.; Lario, P.; Masters, A. P.; Sorensen, T. S.; Sun, F. *Can. J. Chem.* **1993**, *71*, 1910.

(2) Such species are called oxyallyls, because they are often written as zwitterions, with a negatively charged oxygen, singly bonded to C-2 of an allylic cation. However, several lines of evidence indicate that oxyallyls are probably better described as 1,3-diradicals, with a carbonyl group at C-2, than as zwitterions. (a) Osamura, Y.; Borden, W. T.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 5112. (b) Coolidge, M. B.; Yamashita, K.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1751. (c) Lim, D.; Hrovat, D. A.; Borden, W. T.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1994**, *116*, 3494.

(3) Rauk, A.; Sorensen, T. S.; Sun, F. *J. Am. Chem. Soc.* **1995**, *117*, 4506.

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(5) Ichimura, A. S.; Lahti, P. M.; Matlin, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2868.

(6) Powell, H. K.; Borden, W. T. *J. Org. Chem.* **1995**, *60*, 2654.

(7) 2,3-Di-*tert*-butylcyclopropanone has also been prepared and isolated. Sorensen, T. S.; Sun, F. *J. Am. Chem. Soc.* **1995**, *117*, 5592.

(8) Sorensen, T. S.; Sun, F. *Can. J. Chem.* **1996**, *74*, 79.

(9) Heats of formation (from Cox, J. P.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970) show that hydrogen addition to bicyclo[1.1.0]butane to form cyclobutane is more exothermic by 6.5 kcal/mol than hydrogen addition to bicyclo[3.1.0]hexane to form cyclohexane.

S0002-7863(95)04296-X CCC: $12.00

Table 1. CASSCF and CASPT2N/6-31G* Energies (kcal/mol) of Singlet Oxyallyl Diradicals and Transition States Relative to the Isomeric Bicyclo[*n*.1.0]alkanones and CASSCF/6-31G* Zero-Point Energy Corrections

compd	CASSCF	CASPT2N	ΔZPE
1a	0.0[a]	0.0[b]	0.0[c]
4a	20.7	28.9	−1.3
2a	0.0[d]	0.0[e]	0.0[f]
5a	−3.9	−1.3	−1.4
TS for **2a** → **5a**	2.4	3.2	−1.0
3a (boat)	0.0[g]	0.0[h]	0.0[i]
3a (chair)	3.5	3.8	−0.2
TS for **3a** (boat) → **3a** (chair)	4.3	5.3	−0.2
6a	19.0	24.4	−1.9
TS for **6a** → **3a** (boat)	19.2	23.3	−2.1
TS for **6a** → **3a** (chair)	21.6	25.6	−2.0
1b	0.0[j]	0.0[k] (0.0)[l,m]	(0.0)[l,n]
4b	13.9	19.9 (19.5)	(−1.2)
2b	0.0[o]	0.0[p]	
5b	−8.5	−8.1	
3b (boat)	0.0[q]	0.0[r] (0.0)[l,s]	
3b (chair)	4.2	4.8	
6b	13.9	15.3 (15.2)	
TS for **6b** → **3b** (boat)	17.7	19.1	
1c		(0.0)[l,t]	
4c		(18.9)	
3c (boat)		(0.0)[l,u]	
6c		(10.1)	

[a] Relative to −228.6082 hartrees. [b] Relative to −229.2661 hartrees. [c] Relative to 45.2 kcal/mol. [d] Relative to −267.6484 hartrees. [e] Relative to −268.4353 hartrees. [f] Relative to 65.3 kcal/mol. [g] Relative to −306.7197 hartrees. [h] Relative to −307.6455 hartrees. [i] Relative to 85.5 kcal/mol. [j] Relative to −306.6900 hartrees. [k] Relative to −307.6241 hartrees. [l] Energies in parentheses obtained from DFT geometry optimizations at the Becke 3LYP/6-31G* level. [m] Relative to −308.6022 hartrees. [n] Relative to 78.0 kcal/mol. [o] Relative to −345.7298 hartrees. [p] Relative to −346.7946 hartrees. [q] Relative to −384.7957 hartrees. [r] Relative to −385.9997 hartrees. [s] Relative to −387.2540 hartrees. [t] Relative to −544.4821 hartrees. [u] Relative to −623.1155 hartrees.

Computational Methodology

The geometries of **1**−**3** and **4**−**6** were optimized with the 6-31G* basis set[10] at the complete active space (CAS)SCF level of theory. The active space consisted of four electrons in four orbitals. For **1**−**3** the four orbitals were the π and π^* orbitals of the carbonyl group and the σ and σ^* orbitals of the scissile C−C bond; for **4**−**6** they were the four oxyallyl π orbitals.[2a] Vibrational analyses at the (4/4)-CASSCF/6-31G* level of theory were used to identify optimized geometries as minima or transition states and to obtain frequencies for zero-point energy (ZPE) corrections. The CASSCF calculations were carried out with the Gaussian 92 package of *ab initio* programs.[11] The CASSCF/6-31G* optimized geometries are available as supporting information.[12]

Dynamic electron correlation was included by performing single-point CASPT2N calculations[13] at all the CASSCF stationary points. CASPT2N uses second-order perturbation theory to provide electron correlation beyond that included at the CASSCF level. The CASPT2N calculations were carried out using MOLCAS.[14]

Results and Discussion

Ring Opening in Bicyclo[*n*.1.0]alkanones 1a−3a. Table 1 gives the CASSCF and CASPT2N/6-31G* energies of each oxyallyl diradical (**4a**−**6a**), relative to the isomeric bicyclic ketone (**1a**−**3a**). The difference between the CASSCF/6-31G* zero-point vibrational energy (ΔZPE) of each oxyallyl diradical and each bicyclic ketone is also provided in Table 1.

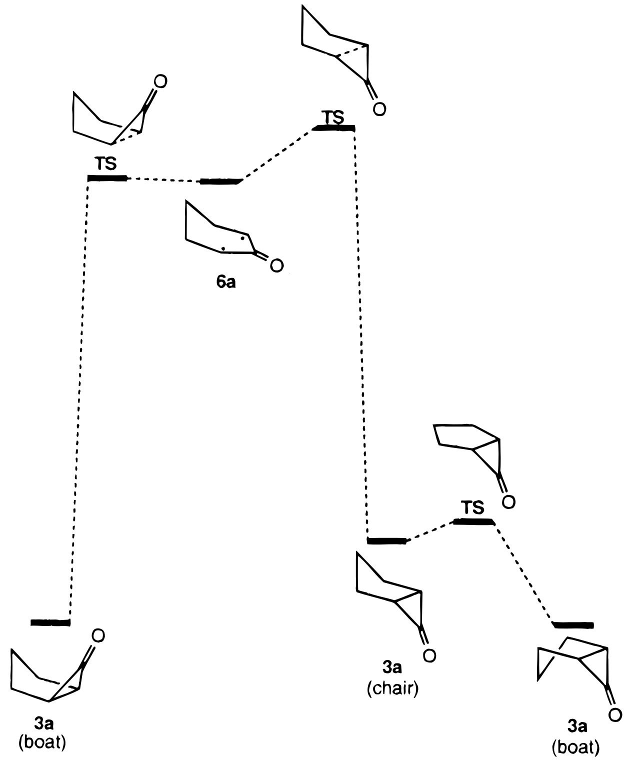

Figure 1. Schematic depiction of the potential surface for ring inversion in **3a**.

The relative energies of the diradicals in Table 1 are consistently higher at the CASPT2N level than at the CASSCF level. CASPT2N selectively stabilizes the bicyclic ketones because it provides correlation for the electrons in all of the strained σ bonds of each three-membered ring. The electron pair in only one of these bonds is correlated at the CASSCF level.

Vibrational analysis found that planar **4a** is the transition state for ring inversion of **1a**.[15] After correction for the difference in zero-point energies (ΔZPE), the CASPT2N/6-31G* energy of **4a** is 27.6 kcal/mol higher than that of **1a**. CASPT2N calculations with the much larger 6-311G(2d,p) basis set[16] reduce the energy difference between **1a** and **4a**, but only by 1.5 kcal/mol.

Unlike diradical **4a**, but like the parent oxyallyl diradical (propan-2-one-1,3-diyl),[2c] **5a**[6] and **6a** are both minima on their potential surfaces. Since **5a** is planar, the same type of transition state must be crossed twice in ring inversion of **2a**, once in ring opening to **5a** and again in ring closure from **5a**. This transition state has been located previously,[6] and its energy, relative to that of **2a** is given in Table 1.

Since **6a** is not planar, the potential surface for ring inversion of **3a** is more complicated than the potential surfaces for ring inversion of **1a** or **2a**. In fact, as shown in Figure 1, **3a** has two conformational minima, a pseudo-chair and a pseudo-boat. The three-membered ring in **3a** causes the former conformation to suffer eclipsing interactions that are absent in cyclohexane. Consequently, as is found to be the case experimentally,[8] the

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(10) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(11) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, W. P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, D.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Steward, J. J. P.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1992.

(12) Ordering information is given on any current masthead page.

(13) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(14) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Seigbahn, P. E. M.; Urban, M.; Widmark, P.-O. MOLCAS; Version 3, University of Lund, Sweden, 1994.

(15) This appears also to be the case at the CASPT2N/6-31G* level, since a small distortion of **4a** along the vibrational coordinate with the imaginary CASSCF frequency also lowered the CASPT2N energy.

(16) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

pseudo-boat is the lower of the two conformations. Its CASPT2N energy, which is given in Table 1, is 3.6 kcal/mol lower than that of the pseudo-chair after ΔZPE correction.

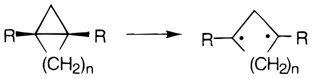
The two conformations are interconverted by passage of the five-membered ring in **3a** through a planar geometry. The transition state for this process has been located and its CASPT2N energy is computed to be only 1.5 kcal/mol greater than that of the pseudo-chair. Obviously, there is only a small barrier to interconversion of the pseudo-chair to the pseudo-boat conformation of **3a**.

As depicted in Figure 1, ring inversion in **3a** involves passage from a pseudo-boat to a ring-inverted pseudo-chair via **6a**.[17] Consequently, two different transition states connect **3a** to **6a**. Both transition states have been located at the CASSCF level. They differ in energy by 2.4 kcal/mol, with the transition state that connects **6a** to the pseudo-chair the higher of the two.

At the CASSCF level a barrier of only 0.2 kcal/mol prevents the closure of **6a** to the pseudo-boat; and at the CASPT2N level, this small barrier to ring closure disappears. Therefore, at the CASPT2N level of theory **6a** may not lie in even a shallow potential well; and ring inversion of **3a** may take place over a single chair transition state. After a small correction for ΔZPE, this transition state lies 25.8 kcal/mol above the pseudo-boat conformation of **3a** at the CASPT2N/6-31G* level of theory.

In good agreement with the experimental results for di-*tert*-butyl derivatives **1c** and **3c**, the CASPT2N energy required to cross the transition state for ring inversion is computed, after ΔZPE corrections, to be 4.0 kcal/mol higher in **1a** than in **3a**. As noted in the introduction, this result is rather surprising, since the cleavage of the bond between the bridgehead carbons of the bicyclo[1.1.0]butane ring system should relieve considerably more strain and, hence, require less energy than breaking the analogous C−C bond in the bicyclo[3.1.0]hexane ring system.[9]

Comparison with Ring Opening in Bicyclo[*n*.1.0]alkanes 7a−9a. In order to verify the correctness of this assumption, we computed the energies of the bicyclo[*n*.1.0]alkanes with *n* = 1−3 (**7a**−**9a**) and the energies of the diradicals (**10a**−**12a**) formed from them. The relative energies for each pair are given in Table 2.



7, n = 1
8, n = 2
9, n = 3
a, R = H
b, R = CH_3
c, R = $C(CH_3)_3$

10, n = 1
11, n = 2
12, n = 3
a, R = H
b, R = CH_3
c, R = $C(CH_3)_3$

Previous (10/10)-CASSCF/6-31G* calculations have found planar **10a** to be the transition state for ring inversion of **7a**.[18] Starting from the (10/10)-CASSCF wave function, CASPT2N calculations gave an energy difference between **7a** and **10a** of 51.8 kcal/mol, which was reduced to 48.2 kcal/mol after corrections for zero-point energies. The former value is nearly the same as the CASPT2N energy difference in Table 2, which is based on a (2/2)-CASSCF reference wave function; and the latter value is in excellent agreement with estimates of this energy difference, derived from experimental data.[19]

Table 2. CASSCF and CASPT2N/6-31G* Energies (kcal/mol) of Singlet Cycloalkane-1,3-diyls, Relative to the Isomeric Bicyclo[*n*.1.0]alkanes

compd	CASSCF	CASPT2N
7a	0.0[a]	0.0[b]
10a	40.5[c]	51.5
8a	0.0[d]	0.0[e]
11a	27.6[f]	36.3
9a (boat)	0.0[g]	0.0[h]
9a (chair)	3.4	3.7
12a	47.3	58.7
TS for **9a** (boat) → **9a** (chair)	3.6	4.3
TS for **12a** → **9a** (boat)	50.2	60.4
TS for **12a** → **9a** (chair)	48.3	58.8
7b	0.0[i]	0.0[j]
10b	39.2	49.1

[a] Relative to −154.8883 hartrees. [b] Relative to −155.4083 hartrees. [c] The D_{2h} structure is not an energy minimum on the (2/2)CASSCF/6-31G* surface, see ref 18. [d] Relative to −193.9449 hartrees. [e] Relative to −194.5983 hartrees. [f] The C_{2v} structure is not an energy minimum on the (2/2)CASSCF/6-31G* surface, see ref 21. [g] Relative to −233.0177 hartrees. [h] Relative to −233.8098 hartrees. [i] Relative to −232.9678 hartrees. [j] Relative to −233.7624 hartrees.

Unlike **7a** and **10a**, in whose dominant configurations all the MOs have the same symmetry, opening of **8a** to **11a** involves a change in the symmetry of the HOMO in the dominant configuration.[20] Consequently a small energy barrier separates **8a** and **11a**.[21] The CASPT2N/6-31G* value in Table 2 for the energy difference between **8a** and **11a**[22] is close to the CI value obtained with a different basis set;[21] and after vibrational corrections,[22] the CASPT2N barrier to ring opening of **8** is close to the experimental value[23] for ring inversion in a simple derivative.

The energy surface for ring inversion in **9a** is more complicated than that for **8a**. As in **8a**, ring opening in **9a** involves a change in the symmetry of the HOMO in the dominant configuration,[20] suggesting that diradical **12a** is an intermediate. However, since pseudo-boat and pseudo-chair conformations of **9a** are possible, as in the case of ring inversion of **3a**, a different transition state connects each conformation of **9a** to **12a**.

Although we were mainly interested in comparing the energy difference between **9a** and **12a** with that between **3a** and **6a**, we did locate both the transition states for ring inversion of **9a**. The CASSCF and CASPT2N energies of boat and chair **9a**, the transition state that connects them, and the transition state that connects each of them to diradical **12a** are given in Table 2.

The differences between the energies of the pseudo-boat and pseudo-chair conformations of **9a** are calculated to be about the same size as in **3a**, with the pseudo-boat lower in both the bicyclic hydrocarbon (**9a**) and ketone (**3a**). However, although the transition state that connects oxyallyl **6a** to boat **3a** is lower

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(17) A geometry for **6a** with a planar carbon skeleton and, hence, C_{2v} symmetry would connect a pseudo-boat or a pseudo-chair conformation of **3a** directly with the identical conformation in ring-inverted **3a**. However, such a C_{2v} geometry must be a mountain top, rather than a saddle point, on the potential energy surface; and we calculate that the CASPT2N energy of this geometry of **6a** is 7.6 kcal/mol higher in energy than the transition state that connects the equilibrium geometry of **6a** with a pseudo-chair conformation of **3a**.

(18) Nguyen, K. A.; Gordon, M. S.; Boatz, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 9241. However, at the TCSCF level, the D_{2h} geometry has two negative force constants, and the transition state has only C_s symmetry.

(19) Chang, M. H.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 4211.

(20) As in the case of the trimethylene diradical (Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475), mixing of the AOs at C-1 and C-3 with the orbitals of the C−H bonds at C-2 in cycloalkane-1,3-diyls destabilizes the S combination of AOs, relative to the A combination. However, in planar cyclobutane-1,3-diyl (**9a**) through-space interaction between the AOs at C-1 and C-3 keeps S below A.[18]

(21) Sherrill, C. D.; Seidl, E. T.; Schaefer, H. F. *J. Phys. Chem.* **1992**, *96*, 3712. At the TCSCF level a C_{2v} geometry for **11a** is not the energy minimum but is very close to it in energy.

(22) Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 5425.

(23) Baldwin, J. E.; Ollerenshaw, J. *J. Org. Chem.* **1981**, *46*, 2116.

Table 3. Energies (kcal/mol) of Some Isodesmic Reactions, Calculated at the CASSCF and CASPT2N Levels of Theory and by DFT[a]

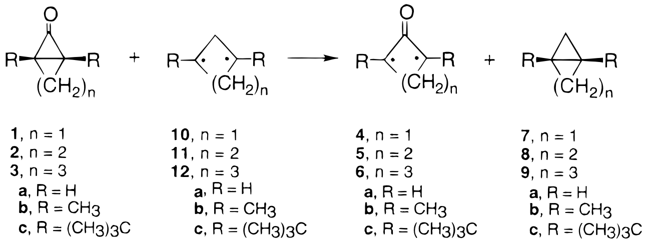
eq no.	reaction	Δ*E*(CASSCF)	Δ*E*(CASPT2N)
1	**1a** + **10a** → **4a** + **7a**	−19.8	−22.6
2	**2a** + **11a** → **5a** + **8a**	−31.5	−37.6
3	**3a** + **12a** → **6a** + **9a**	−28.5	−34.3
4	**4a** + **11a** → **5a** + **10a**	−1.5	−1.9
5	**5a** + **12a** → **6a** + **11a**	4.2	4.2
6	**1a** + **8a** → **2a** + **7a**	10.2	13.1
7	**1a** + **9a** → **3a** + **7a**	11.4	14.0
8	**1a** + **2b** → **1b** + **2a**	−0.3	0.8
9	**4a** + **5b** → **4b** + **5a**	−2.5	−1.4
10	**1a** + **3b** → **1b** + **3a**	−3.4	−2.2
11	**4a** + **6b** → **4b** + **6a**	−2.9	−2.3
12	**1b** + **3c** → **1c** + **3b**		−11.5[b]
13	**4b** + **6c** → **4c** + **6b**		−7.1[b]

[a] Becke 3LYP/6-31G* calculations. [b] DFT result.

in energy than the transition state that leads from **6a** to chair **3a**, the reverse is true of the two transition states that connect diradical **12a** to the boat and chair conformations of **9a**. The lower energy transition state leads to the higher energy, chair conformation of bicyclo[3.1.0]hexane (**9a**).

The results in Table 2 confirm the supposition, based on heats of formation,[9] that the energy difference between bicyclo[1.1.0]butane (**7a**) and cyclobutane-1,3-diyl (**10a**) is smaller by ≈7 kcal/mol than the energy difference between pseudo-boat bicyclo[3.1.0]hexane (**9a**) and cyclohexane-1,3-diyl (**12a**). Therefore, greater relief of strain upon cleavage of the bond between the bridgehead carbons in the bicyclo[*n*.1.0] ring system for $n = 3$ than for $n = 1$ cannot be the reason the CASPT2N energy difference between **1a** and **4a** is *larger* than that between **3a** and **6a** by ≈5 kcal/mol. One must thus conclude that, for some reason, introduction of a carbonyl group into bicyclo[1.1.0]butane (**7a**), to form **1a**, has a much smaller effect on weakening the C−C bond between the bridgehead carbons than does introduction of a carbonyl group into bicyclo[3.1.0]hexane (**9a**), to form **3a**.

Weakening of the Bonds between the Bridgehead Carbons by Carbonyl Groups. The energies in Tables 1 and 2 can be used to compute the effect of a carbonyl group on reducing the energy required to break the bond between the bridgehead carbons in a bicyclo[*n*.1.0]alkane. The bond-weakening effects of the carbonyls in **1a**−**3a** are given, respectively, by the energies of the series of isodesmic[24] reactions,



The energies of these reactions for $n = 1-3$ and R = H are given by eqs 1−3 of Table 3 and are shown at both the CASSCF and CASPT2N levels.

The greatest effect of the presence of a carbonyl group is seen in eq 2, which gives the energetics of bridgehead bond cleavage in **2a**, compared to **8a**. The carbonyl group in **2a**/**5a** reduces the energy difference between the ring-opened and ring-closed geometries of bicyclo[2.1.0]pentane (**8a**) by 31.5 kcal/mol at the CASSCF level and by 37.6 kcal/mol at CASPT2N. The diradical stabilization energy provided by the carbonyl group is expected to be larger at the CASPT2N than at the CASSCF level, since provision of dynamic electron correlation enhances the effects of electron delocalization.[25]

The weakening of the bridgehead C−C bond by the carbonyl group in **2a**/**5a** is about 3 kcal/mol greater than that computed for **3a**/**6a**. Some of this small energy difference is associated with the cost of achieving a geometry in which the p AOs at the two radical centers overlap maximally with the π orbitals of the carbonyl group in 2-cyclohexanone-1,3-diyl (**6a**). This requires some flattening of the six-membered ring in **6a**, compared to that in cyclohexane-1,3-diyl (**12a**). In contrast, the carbons of the five-membered ring in cyclopentane-1,3-diyl (**11a**) all lie in the same plane. Thus, upon introducing an oxygen at C-2 to form **5a**, there is no energetic cost associated with achieving a geometry in which π overlap is maximized.

The energetic price to be paid for achieving such a geometry upon introduction of an oxygen at C-2 of **12a** to form **6a** can be estimated by recalculating the energy of **12a** with five of the six carbons constrained to lie in the same plane, as they do in **6a**. The CASSCF energy of **12a** is found to increase by 1.6 kcal/mol, indicating that ring flattening in **6a** accounts for only part of the difference in energies between the isodesmic reactions in eqs 2 and 3 of Table 3.

The remainder is probably associated with the smaller $C_1-C_2-C_3$ bond angles in **5a** and **11a** (respectively, 103.8° and 102.6°) than in **6a** and **12a** (respectively, 114.3° and 113.7°), which make the C_1-C_3 distance smaller in the five- than in the six-membered ring diradicals. On carbonyl group introduction, the through-space interaction between the p-π AOs at C_1 and C_3 changes from antibonding to bonding, as the dominant interaction of the S combination of these AOs changes from being with a filled combination of C−H bonding orbitals at C_2 in the hydrocarbon diradicals[20] to the unfilled π^* orbital of the carbonyl groups in the oxyallyl diradicals.[26] Consequently, the greater through-space interaction between the p-π AOs at C_1 and C_3 of the five-membered ring diradicals causes carbonyl group introduction at C_2 to have a greater stabilizing effect on **11a** than on **12a**.

Much more striking than the small difference between the energies of the isodesmic reactions in eqs 2 and 3 is the large difference between the energies of the isodesmic reactions in eqs 1 and 2. The latter difference amounts to 11.7 kcal/mol at the CASSCF level and 15.0 kcal/mol at the CASPT2N level. This large difference indicates that introduction of a carbonyl group at C-5 of bicyclo[2.1.0]pentane (**8a**), to form **2a**, has a much larger effect on weakening the bond between the bridgehead carbons than introduction of a carbonyl group at C-2 of bicyclo[1.1.0]butane (**7a**), to form **1a**.

The difference between the energies of the isodesmic reactions in eqs 1 and 3 is only 3 kcal/mol less than the difference between the energies of the reactions in eqs 1 and 2. The large differences between the energies of the isodesmic reaction in eq 1 and those in both eqs 2 and 3 indicate that it is the reaction in eq 1 that is unusual and that introduction of a carbonyl group into the three-membered ring has a much smaller effect on weakening the bond between the bridgehead carbons in bicyclo[1.1.0]butane (**7a**) than in bicyclo[2.1.0]pentane (**8a**) or bicyclo[3.1.0]hexane (**9a**).

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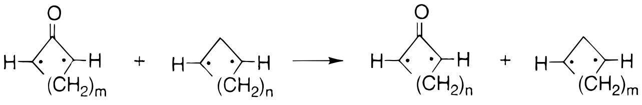
[24] Hehre, W. J.; Radom, L.; Schleyer, P. von R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 271−324.

[25] Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783. Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

[26] This change in the dominant interaction between the S combination of p-π AOs at C_1 and C_3 and the π orbitals at C_2 is responsible for the S combination being higher in energy than the A combination in **11a** and **12a**[20] but considerably lower than S in **5a** and **6a**.[2]

Diradical Stabilization Energies. One possible explanation for the large difference between the energy of the isodesmic reaction in eq 1 and those in eqs 2 and 3 is that introduction of a carbonyl group into cyclobutane-1,3-diyl (**10a**) to form oxyallyl **4a** provides less stabilization for the diradical than introduction of a carbonyl group into either cyclopentane-1,3-diyl (**11a**) to form oxyallyl **5a** or into cyclohexane-1,3-diyl (**12a**) to form oxyallyl **6a**. Upon carbonyl group introduction, the difference between the diradical stabilization energies in different sized rings is given by the isodesmic reactions



4a, m = 1 **10a**, n = 2 **5a**, n = 2 **10a**, m = 1
5a, m = 2 **12a**, n = 3 **6a**, n = 3 **11a**, m = 2

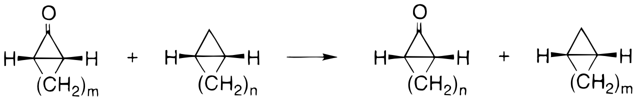
The energies of these reactions are given by eqs 4 and 5 of Table 3.

Table 3 shows that the isodesmic reaction in eq 4 is slightly exothermic, indicating that carbonyl group introduction into cyclopentane-1,3-diyl (**11a**) provides about 2 kcal/mol more stabilization than carbonyl group introduction into cyclobutane-1,3-diyl (**10a**). A plausible explanation for this difference is that introduction of a third trigonal carbon into the five-membered ring of **11a** causes an increase in strain energy that is less by about 2 kcal/mol than that which results from introduction of a third trigonal carbon into the four-membered ring of **10a**.

Table 3 also shows that the reaction in eq 5 is endothermic by about 4 kcal/mol, indicating that carbonyl group introduction at C-2 provides this much more stabilization for cyclopentane-1,3-diyl (**11a**) than for cyclohexane-1,3-diyl (**12a**). This finding provides support for the proposal, given in the previous section, that the difference between the energies of the reactions in eqs 2 and 3 is primarily associated with the differential effects of carbonyl group introduction on diradicals **11a** and **12a**, rather than on bicyclic alkanes **8a** and **9a**.

The energies of the isodemic reactions in eqs 4 and 5 are both small and are easily explained. Obviously, the differences in radical stabilization energies upon carbonyl group introduction do not account for the much larger differences between the energy of the reaction in eq 1 and the energies of those in eqs 2 and 3. Therefore, the explanation of why introduction of a carbonyl group at C-2 of bicyclo[1.1.0]butane (**7a**) has an anomalously small effect on weakening the bond between the bridgehead carbons cannot be that the carbonyl group in 2-cyclobutanone-1,3-diyl (**4a**) provides an anomalously small amount of stabilization for this diradical. In fact, adding eqs 4 and 5 shows that carbonyl group introduction provides about 2 kcal/mol *more* stabilization for cyclobutane-1,3-diyl (**10a**) than for cyclohexane-1,3-diyl (**12a**).

Effects of Carbonyl Group Introduction on Bicyclo[*n*.1.0]-alkanes. Since the large differences between the energy of the isodesmic reaction in eq 1 and the energies of those in eqs 2 and 3 of Table 3 are not due to the carbonyl group in 2-cyclobutanone-1,3-diyl (**4a**) providing an anomalously small amount of stabilization for this diradical, these differences must be due to the carbonyl group in bicyclo[1.1.0]butan-2-one (**1a**) providing an anomalously large amount of stabilization for this bicyclic ketone. In fact, taking the difference between eqs 1 and 2 and adding eq 4 to it demonstrates that the difference between the energies of the reactions in eqs 1 and 2 must largely come from the energy of the isodesmic reaction



1a, m = 1 **8a**, n = 2 **2a**, n = 2 **7a**, m = 1
1a, m = 1 **9a**, n = 3 **3a**, n = 3 **7a**, m = 1

with $m = 1$ and $n = 2$. The energy of this reaction is given by eq 6 of Table 3. Similarly, the difference between the energies of the reactions in eqs 1 and 3 must largely come from the energy of the same isodesmic reaction but with $n = 3$. The energy of the latter reaction is given by eq 7.

As shown in Table 3, the reaction in eq 6 is endothermic by 10.2 kcal/mol at the CASSCF level and by 13.1 kcal/mol at the CASPT2N level of theory. The reaction in eq 7 is endothermic by about the same amounts. The substantial endothermicities of the reactions in both eqs 6 and 7 indicate that introduction of a carbonyl group is much more favorable in bicyclo[1.1.0]-butane (**7a**) than in bicyclo[2.1.0]pentane (**8a**) or bicyclo[3.1.0]-hexane (**9a**). We attribute this computational result to a highly stabilizing interaction between the π^* orbital of the carbonyl group and the bent bond between the bridgehead carbons in bicyclo[1.1.0]butan-2-one (**1a**).

Evidence for the existence of such an interaction in the geometry calculated for **1b** has previously been discussed.[3] As in the Becke 3LYP/6-31G* optimized geometry of **1b**, in the CASSCF/6-31G* optimized geometry of **1a** the bond between the bridgehead carbons in **1a** is unusually long (1.658 Å), especially in comparison to the length of this bond (1.506 Å) in the hydrocarbon (**7**). In addition, the bonds between the bridgeheads and the carbonyl carbon in **1a** are unusually short (1.449 Å), compared to the lengths of these bonds (1.489 Å) in **7a**. Finally, the carbonyl carbon in **1a** is pyramidalized ($\phi = 9.2°$)[27] in such a manner as to increase its interaction with the bent bond between C-1 and C-3.

Experimental evidence for a strong interaction between the carbonyl group and the bent bond between the bridgehead carbons in **1b** and **1c** is provided by spectroscopic data, both ^{13}C NMR and IR.[3] We also believe that this interaction is largely responsible for the apparently anomalous experimental energetics of ring inversion of **1c** and **3c**. As noted in the introduction, despite the 6.5 kcal/mol larger amount of strain energy released upon cleavage of the bond between the bridgehead carbons in bicyclo[1.1.0]butane (**7a**) than in bicyclo-[3.1.0]hexane (**9a**),[9] the free energy of activation for ring inversion found in **1c**[3] is 5 kcal/mol higher than that measured in **3c**.[8] A substantial amount of this 11.5 kcal/mol difference between what might have been expected from the experimental strain energies of bicyclic hydrocarbons **7a** and **9a** and the barriers to ring inversion, measured in bicyclic ketones **1c** and **3c**, we attribute to the stabilization of **1c** by the interaction between the bent bond of bicyclobutane and the π^* orbital of the carbonyl group.

The CASSCF bond length between the bridgehead carbons is actually slightly greater in **2a** (1.677 Å) than in **1a** (1.658 Å), and the carbonyl carbon slightly more pyramidalized ($\phi = 10.0°$ in **2a**, compared to $\phi = 9.2°$ in **1a**). However, if construed as reflecting the amount of interaction between the bridgehead C−C bond and the π^* orbital of the carbonyl group, these geometrical comparisons are obviously misleading. The very large positive energy of the isodesmic reaction in eq 6 indicates

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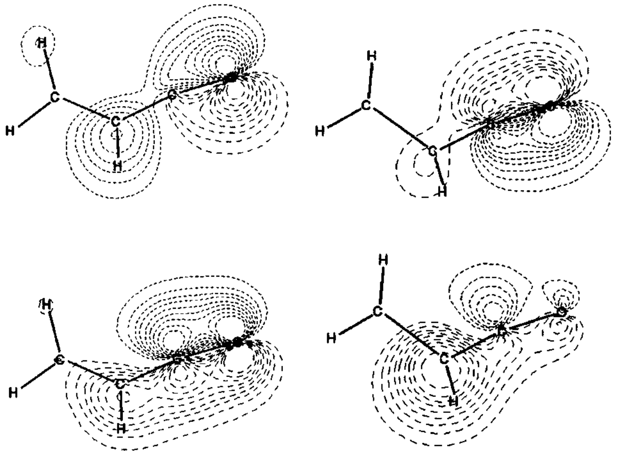
(27) The pyramidalization angle, ϕ, is the angle between the plane containing the carbonyl carbon and bridgehead carbons and the extension of the O−C bond.



1a **2a**

Figure 2. Contour plots of the π_{CO} and σ_{CC} MOs in bicyclic ketones **1a** and **2a**. Plots are in the C_s symmetry plane that contains the carbonyl group of **1a** and **2a** and the methylene group of **1a**. Atoms that do not lie in this plane have been projected onto it for the sake of clarity.

that the interaction of the bridgehead C−C bond with the π^* orbital of the carbonyl group is much less stabilizing in **2a** than in **1a**.[28]

The reason for this difference between **1a** and **2a** is that the bond between the bridgehead carbons has much less π-like character in **2a** than in **1a**. Consequently, this bond in **2a** interacts much less strongly than the bond in **1a** with the π^* orbital of the carbonyl group. This can be seen in Figure 2, which shows plots of the MOs that comprise the bridgehead C−C and carbonyl C−O π bonds in **1a** and **2a**. Figure 2 reveals much more mixing between the bond between the bridgehead carbons and the carbonyl group in **1a** than in **2a**.[29]

Effects of Alkyl Groups at the Bridgehead Carbons on the Ring Opening of Bicyclo[*n*.1.0]alkanones. The CASPT2N barriers to ring inversion of **1a** and **3a** in Table 1 are both considerably larger than those measured for the di-*tert*-butyl derivatives (**1c**[3] and **3c**[8]). Assuming that the calculated barriers for **1a** and **3a** are not significantly in error, the lower barriers for **1c** and **3c** could be due to destabilization of the bicyclic ketones by steric repulsions between the bulky *tert*-butyl groups, to stabilization of the transition states for ring inversion (**4c** and **6c**) by these alkyl substituents, or to a combination of both of these two effects.

In order to assess the relative importance of diradical stabilization and bicyclic ketone destabilization, we calculated the effects of the bridgehead methyl groups in **1b**−**3b** on reducing the strengths of the bonds between the bridgehead carbons in **1a**−**3a**. Although the steric repulsions between the methyl groups in **1b**−**3b** should be smaller than those between the *tert*-butyl groups in **1c**−**3c**, the stabilization of oxyallyl diradicals **4**−**6** by the two different types of alkyl groups would be expected to be rather similar.

The geometries of **1b**−**3b** and **6b** were optimized in C_s symmetry. The geometries of **4b** and **5b** were optimized in C_{2v} symmetry, with the two methyl C−H bonds that lie in the plane of the carbons pointed toward the carbonyl group in each oxyallyl diradical. Calculations on **4b** and **5b**, in which these C−H bonds were rotated by 180°, gave CASSCF energies that were higher by respectively 1.5 and 0.8 kcal/mol.

The energies of **1b**−**6b** are given in Table 1. The methyl groups in **1b** are computed to reduce the CASPT2N barrier to ring inversion by 9.0 kcal/mol from that in **1a**. If the ΔZPE = −1.3 kcal/mol correction for ring inversion of **1a** is applied to the barrier calculated in **1b**,[30] a barrier of 18.6 kcal/mol is predicted. This is only slightly higher than the value of $\Delta H^{\ddagger} = 16 \pm 1$ kcal/mol for ring inversion measured in **1c**.[3] This result suggests that steric repulsions between the *tert*-butyl groups in **1c** have a relatively minor effect on the size of the barrier to ring inversion in this bicyclic ketone.

Supporting evidence for this conclusion comes from the results of Becke3LYP/6-31G* density functional calculations.[31] Use of density functional rather than *ab initio* methodology enabled the energy difference between **1c** and **4c** to be computed. As shown in Table 1, without zero-point corrections, a value of 18.9 kcal/mol was obtained for the barrier to ring inversion in the 1,3-di-*tert*-butyl derivative (**1c**) of **1a**, in good agreement with experiment.[3]

Also as shown in Table 1, at the Becke3LYP/6-31G* level the energy difference between **1b** and **4b** is calculated to be 19.5 kcal/mol, which is in excellent agreement with the CASPT2N value and only 0.6 kcal/mol larger than the Becke3LYP/6-31G* energy difference between **1c** and **4c**. The finding that the calculated barriers to ring inversion in the 1,3-dimethyl (**1b**) and 1,3-di-*tert*-butyl (**1c**) derivatives of **1a** are nearly the same indicates that steric destabilization of **1c** by the bridgehead *tert*-butyl groups plays a very minor role in reducing the barrier to ring inversion in **1c** from that calculated for **1a**.

The absence of significant steric destabilization of **1c** is easy to rationalize. The large angles formed by the bond between the bridgehead carbons and the substituents attached to these carbons in bicyclo[1.1.0]butan-2-ones (**1**) cause bulky bridgehead substituents to interact with each other significantly less in **1** than in either *cis*-disubstituted cyclopropanones[7] or bicyclo[3.1.0]hexan-2-ones (**3**) (*vide infra*).

The finding that the calculated barriers to ring inversion in **1b** and **1c** are both lower than the barrier in **1a** by the same amount indicates that this energy lowering must be due to stabilization of oxyallyl diradicals **4b** and **4c** by the alkyl groups at C-1 and C-3. Alkyl group stabilization of oxyallyl diradical **4** is quite large. For example, as noted above, the methyl groups in **1b** make the CASPT2N energy difference between it and **4b** 9.0 kcal/mol smaller than the energy difference between **1a** and **4a**.

A fruitful comparison of the stabilizing effect of the methyl groups in **4b** is with the effect of bridgehead methyl groups on lowering the barrier for ring inversion in bicyclo[1.1.0]butane (**7a**). As shown in Table 2, the methyl groups in **7b** and **10b** make the CASPT2N energy difference between them only 2.4 kcal/mol smaller than the CASPT2N energy difference between bicyclo[1.1.0]butane (**7a**) and cyclobutane-1,3-diyl (**10a**). Thus,

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[28] There may be a very small amount of stabilizing interaction between the bond between the bridgehead carbons and π^* of the carbonyl group in bicyclo[2.1.0]pentan-5-one (**2a**). The difference between creating a carbonyl group in the one-carbon bridge of bicyclo[2.1.0]pentane (**8a**) and of bicyclo-[3.1.0]hexane (**9a**) is given by the difference between eqs 6 and 7. This difference amounts to roughly 1 kcal/mol at both the CASSCF and CASPT2N levels of theory. One interpretation of this finding is that 1 kcal/mol represents the amount of energy by which an interaction of the bond between the bridgehead carbons and the carbonyl group stabilizes **2a**, relative to **3a**.

[29] In the higher energy of the two MOs for **1a**, the bridgehead C−C bond mixes in an antibonding fashion with the π orbital of the carbonyl group but in a bonding fashion with π^*. The net effect of these two interactions is to cause the carbonyl carbon's contribution to the resulting MO to be relatively small and that of the oxygen to be relatively large.

[30] Since the major purpose of these calculations was to simply assess the effect of the methyl substituents on the energy difference between bicyclo[*n*.1.0]alkanones **1**−**3** and the corresponding oxyallyl diradicals (**4**−**6**), CASSCF/6-31G* zero-point corrections were not calculated for the energies of **1b**−**6b**. However, as shown in Table 1, Becke3LYP/6-31G*[31] vibrational analyses give nearly the same value of ΔZPE for opening of **1b** to **4b** as CASSCF/6-31G* gives for opening of **1a** to **4a**.

[31] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

bridgehead methyls are calculated to reduce the energy required for ring inversion by 6.6 kcal/mol more in bicyclo[1.1.0]butanone (**1**) than in bicyclo[1.1.0]butane (**7**).

This comparison suggests that methyl groups provide an unusual amount of stabilization for singlet oxyallyl diradicals, compared to singlet hydrocarbon diradicals.[32] This inference is consistent with the previous computational finding that methyl groups at C-1 and C-3 stabilize the singlet state of the parent oxyallyl diradical, relative to the triplet, by about 5 kcal/mol.[2b]

As shown in Table 1, methyl substituents at C-1 and C-3 of **2a** and **5a** selectively stabilize the five-membered oxyallyl diradical, relative to bicyclo[2.1.0]pentan-5-one, by 6.8 kcal/mol at the CASPT2N level. The selective stabilization of the oxyallyl, relative to the bicyclic ketone, by methyl groups is 2.2 kcal/mol less in **2b**/**5b** than in **1b**/**4b** at both the CASSCF and CASPT2N levels of theory.

The energies of isodesmic reactions 8 and 9 in Table 3 show that most of this difference between the effect of methyl substituents on the two ring-opening reactions is found in the oxyallyl diradicals, where methyl substituents stabilize **4** more than **5**. This is not surprising, since in the four-membered ring of **4a** the single CH_2 group of the ring must provide hyperconjugative stabilization for both the radical centers; whereas, in the five-membered ring of **5a** each radical center has an adjacent CH_2 group.

More precisely, if a single-configuration wave function were used, a_2 would be the LUMO of oxyallyl;[2a] so hyperconjugative electron donation into this π orbital is particularly stabilizing. However, the orbitals of the CH_2 group of the ring in **4a** have the wrong symmetry to donate electrons into this MO of oxyallyl. In contrast, there is a combination of orbitals on the two methyl groups in **4b** that does have a_2 symmetry and which can, therefore, provide hyperconjugative stabilization in **4b** of a type that is unavailable in **4a**.

There is also an a_2 combination of filled orbitals on the two CH_2 groups in **5a**. This high-lying filled orbital of the ethano bridge provides hyperconjugative donation into the a_2 π orbital of the oxyallyl group in **5a**. Consequently, methyl substituents at C-1 and C-3 furnish less stabilization for **5b** than for **4b**.

At the CASPT2N level bridgehead methyls reduce the strength of the bond between the bridgehead carbons in **3** by 9.1 kcal/mol, almost the same reduction in bond strength as caused by the bridgehead methyls in **1**. Although the net effect of bridgehead methyl substituents on this bond strength in **3** is about the same as that in **1**, the energies of the isodesmic reactions in eqs 10 and 11 of Table 3 show that the methyl groups do affect the relative energies of bicyclic ketones **1** and **3** and also oxyallyl diradicals **4** and **6**. However, because the effect of the methyl groups is to stabilize **1**, relative to **3**, by 2.2 kcal/mol at the CASPT2N level and to stabilize **4**, relative to **6**, by 2.3 kcal/mol, these two effects are of nearly the same size; so they almost cancel.

The selective stabilization of **1** by introduction of methyl groups is probably due to the very long bond between the bridgehead carbons in **1a** and **1b**,[32] contrasted with the normal C−C bond lengths in **3a** and **3b**. Methyl groups selectively stabilize **4**, relative to **6**, probably for the same reason that they stabilize **4**, relative to **5** (*vide supra*). The near cancellation of these two effects leaves the difference between the strengths of the bridgehead bonds in **1b** and **3b** nearly the same (≈5 kcal/mol) as in **1a** and **3a**. As discussed above, the bicyclo[1.1.0]butan-2-ones (**1**) require more energy for ring inversion than the bicyclo[3.1.0]hexan-6-ones (**3**), due to the stabilizing interaction between the carbonyl group and the bent bond that joins the bridgehead carbons in **1**.

As also noted above, the results of our Becke3LYP/6-31G* DFT calculations indicate that the substitution of *tert*-butyl for methyl has very little effect (0.6 kcal/mol) on weakening the bond between the bridgehead carbons in **1c**, relative to that in **1b**. However, our DFT calculations find that the bond between the bridgehead carbons in **3c** is weakened, relative to that in **3b**, by 5.0 kcal/mol upon substitution of *tert*-butyl for methyl. As shown in Table 1 the energy difference between **3c** and **6c** is computed to be 10.1 kcal/mol,[33] which is in good agreement with the experimental value of $\Delta G^{\ddagger} = 11.5$ kcal/mol for ring inversion in **3c**.[8]

Comparison of the energies of the isodesmic reactions in eqs 12 and 13 of Table 3 shows that substitution of *tert*-butyl for methyl weakens the bond between the bridgehead carbons in **3** more than in **1** by selectively destabilizing bicyclo[3.1.0]hexan-6-one (**3c**), rather than by selectively stabilizing oxyallyl **6c**. In fact, eq 13 shows that the substitution of *tert*-butyl for methyl actually destabilizes **6** by 7.1 kcal/mol more than **4**. The greater destabilization of **6** is easily rationalized by the smaller external bond angles in a six- than in a four-membered ring.

However, as shown by eq 12, the destabilization of **3**, relative to **1**, by the substitution of *tert*-butyl for methyl is 11.5 kcal/mol, which is 4.4 kcal/mol larger than the destabilization of **6**, relative to **4**. We attribute the selective destabilization of **3c** to a strong interaction between the vicinal *tert*-butyl groups in this bicyclo[3.1.0]hexan-6-one. The two bridgehead *tert*-butyl substituents interact more strongly in **3c** than in **1c**, because the angles formed by the bond between the bridgehead carbons and the substituents attached to these carbons are smaller in bicyclo[3.1.0]hexan-6-ones (121.6° in **3a**, 124.6° with CASSCF and 124.8° with DFT in **3b**, and 132.2° in **3c**) than in the corresponding bicyclo[1.1.0]butan-2-ones (126.9° in **1a**, 135.0° with CASSCF and 133.6° with DFT in **1b**, and 142.0° in **1c**). The smaller *tert*-butyl$-C_{bh}-C_{bh}$ bond angles in **3c** than in **1c** result in much more steric destabilization of the former than the latter and, thus, a lowering of the barrier to ring inversion by 4.4 kcal/mol more in **3** than in **1** upon substitution of *tert*-butyl for methyl.[33]

Conclusions

DFT calculations at the Becke3LYP/6-31G* level reproduce satisfactorily the experimental barriers to ring inversion in **1c**[3] and **3c**.[8] The barrier to ring inversion in **1c** is computed to be higher than that in **3c** by 8.8 kcal/mol, which is slightly larger than the measured difference of 5.2 kcal/mol between the free energy barriers to ring inversion in these two, di-*tert*-butylbicycloalkanones.

Of the 8.8 kcal/mol difference between the calculated DFT barriers, 4.4 kcal/mol can be attributed to steric destabilization of **3c**, relative to **1c**, by greater interaction between the bridgehead *tert*-butyl groups in the former bicyclic ketone than in the latter. With methyl rather than *tert*-butyl groups at the bridgeheads, the bond between the bridgehead carbons is

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[32] The size of the differential stabilization provided by the methyl groups in oxyallyl diradical **4b**, relative to hydrocarbon diradical **10b**, is actually greater than 6.6 kcal/mol. Presumably because of the extraordinarily long bonds between the bridgehead carbons in **1a** (1.658 Å) and **1b** (1.649 Å), the methyl groups in **1b** stabilize it relative to bicyclo[1.1.0]butan-2-one (**1a**) by more than the methyl groups in **7b** stabilize it relative to bicyclo[1.1.0]butane (**7a**). This can be seen by calculating the energy of the isodesmic reaction, **1a** + **7b** → **1b** + **7a**, which amounts to −2.4 kcal/mol at the CASPT2N level. The CASPT2N energy of the isodesmic reaction, **4a** + **10b** → **4b** + **10a**, shows that substitution of methyl groups at C-1 and C-3 of 2-cyclobutanone-1,3-diyl (**4a**) and cyclobutane-1,3-diyl (**10a**) actually provides 9.0 kcal/mol more stabilization for the oxyallyl diradical (**4b**) than for the hydrocarbon diradical (**10b**).

[33] At the Becke3LYP/6-31G* level both **6b** and **6c** are transition states, whereas at the CASSCF level **6b** is an intermediate.

calculated to be stronger in **1b** than in **3b** by slightly more than 4 kcal/mol. The methyl groups in **1b** and **3b** reduce the strengths of the bridgehead C−C bonds in both **1a** and **3a** by almost exactly 9 kcal/mol. This reduction is largely due to stabilization by methyl substituents of the oxyallyl diradicals (**4a** and **6a**) formed upon ring opening of respectively **1a** and **3a**.

The finding that the bonds between the bridgehead carbons in both **1a** and **1b** are stronger by about 4 kcal/mol than the corresponding bonds in respectively **3a** and **3c** is surprising. Based on both the calculated strengths of the bridgehead C−C bonds in bicyclic hydrocarbons **7a** and **9a** and the experimental heats of hydrogenation of these bonds,[9] the bridgehead C−C bond in **1a** would be expected to be about 7 kcal/mol weaker than that in **3a**.

The isodesmic reactions in Table 3 indicate that the surprising strength of the bond between bridgehead carbons in **1a**, compared to **3a**, is due to a very stabilizing interaction in **1a** between this bond and the π^* orbital of the carbonyl group. It is this interaction in **1c** that is chiefly responsible for the unexpected experimental finding that the barrier to ring inversion is 5 kcal/mol larger, not 7 kcal/mol smaller, in **1c**[3] than in **3c**.[8]

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Supporting Information Available: CASSCF/6-31G* optimized geometries of **1a**−**12a**, **1b**−**7b**, **10b**, the transition states connecting **2a**, **3a**, and **3b** with respectively **5a**, **6a**, and **6b**, and Becke3LYP/6-31G* optimized geometries for **1b** and **1c**, **3b** and **3c**, **4b** and **4c**, and **6b** and **6c** (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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