Ring Expansion and Contraction of a Two-Carbon Bridged Spiropentane

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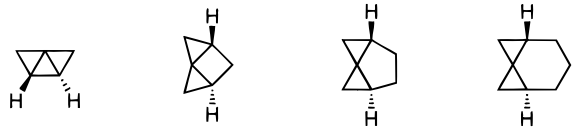
The reactions of tricyclo[4.1.0.0^{1,3}]heptan-4-one (**5**) and two related systems with diazomethane and *m*-CPBA were examined in order to determine the relative reactivity and migratory aptitudes for the three compounds. The reactions of **5** with diazomethane and *m*-CPBA yielded new derivatives of the tricyclo[5.1.0.0^{1,3}]octane ring system that showed that migration of cyclopropylcarbinyl is favored over cyclopropyl migration in this system. Photolysis of 5-diazotricyclo[4.1.0.0^{1,3}]heptan-4-one (**23**) in methanol and dimethylamine did not lead to ring contraction to the tricyclo[3.1.0.0^{1,3}]hexane ring system, but an interesting product was derived from an unusual rearrangement process in the photolysis in dimethylamine. Matrix photolysis of **23** at 15 K gave a decrease in the diazo band at 2085 cm^{-1} and the appearance of a new band at 2117 cm^{-1}, which is a normal position expected for a small-ring ketene such as cyclopropylketene. Thus, matrix photolysis appears to have yielded a derivative of the previously unknown tricyclo[3.1.0.0^{1,3}]hexane ring system. The lithium enolate of **5** was characterized by NMR spectroscopy at −80 °C and was found to rearrange to *m*-cresol at −65 °C. The geometries of the bridged spiropentanes of this work were optimized at the MP2(frozen core)/6-31G* level of theory, and group equivalent values were derived in order to calculate the heats of formation for these compounds using the calculated energies.

1. Introduction

We have been interested in the effects of structural deformation on the structures, properties, and reactions of organic compounds. One set of deformed compounds are the bridged spiropentanes, **1**−**4**. We have reported the preparation of **1** and found it to have a short half-life at −55 °C before rearranging to cyclopentadiene.[1] The two-carbon bridged compounds such as **3** and its derivatives are easily prepared by the intramolecular carbene addition discovered by Skattebøl.[2] The three-carbon bridged hydrocarbon, **4**, has been prepared via a rearrangement,[3] but no derivatives have been reported. Furthermore, no preparation for **2** or its derivatives has been forthcoming. The formation of derivatives of **2** and **4** is the major focus of this work.



1 **2** **3** **4**

Theoretical calculations have proven to be a valuable counterpart to preparative studies.[4] We have previously reported HF/6-31G* calculations[5] for **1**−**4** and MP2/6-31G* calculations for **1**.[6] Dodzuik, Leszczynski, and Nowinski have reported MP2/6-31G** calculations for **1**−**3**.[7] We have now carried out geometry optimizations for **1**−**4** and a number of their derivatives at the MP2/6-31G* theoretical level. This has proven to give structures that are in good agreement with experimental studies.[8] The calculations provide estimates of heats of formation that will be useful in interpreting the results of some of the reactions that were studied.

2. Structures and Energies

The calculated energies are summarized in Table 1, and the more interesting structural data are shown in Figures 1 and 2. It should be noted that **1** has presented a problem in that at the MP2/6-31G* level of theory it is predicted to have a structure that is slightly asymmetric,[4] whereas a symmetrical structure was reported at the MP2/6-31G** level.[7] However, we found the symmetrical MP2/6-31G** structure to be a transition state (one imaginary frequency). The difference in energy between the symmetric and asymmetric structures was negligible (less than 0.1 kcal/mol) and, thus, presents no problem in estimating the heat of formation.

It is usually more convenient to work with heats of formation rather than total energies. We have shown that the HF/6-31G* calculated energies could be converted to heats of formation via a group equivalent approach[5] where 627.5 is the conversion from

$$\Delta H_f = 627.5(E_T - n_{CH_3}E_{CH_3} - n_{CH_2}E_{CH_2} - n_{CH}E_{CH^-} ...)$$

(1) Wiberg, K. B.; McClusky, J. V. *Tetrahedron Lett.* **1987**, *28*, 5411.
(2) Skattebøl, L. *J. Org. Chem.* **1966**, *31*, 2789.
(3) Meibach, T.; Brinker, U. H. *J. Org. Chem.* **1993**, *58*, 6524.
(4) Wiberg, K. B.; McMurdie, N. D.; McClusky, J. V.; Hadad, C. M. *J. Am. Chem. Soc.* **1993**, *115*, 10653. As a result of a typographical error, the structure of **1** appeared to be more unsymmetrical than calculated. The structure shown in Figure 1 is correct.
(5) Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285.
(6) McClusky, J. V. Ph.D. Thesis, Yale University, 1988.
(7) Dodziuk, H.; Leszczynski, Jerzy, Nowinski, K. S. *J. Org. Chem.* **1995**, *60*, 6860.
(8) Hehre, W. J.; Radom, L.; Scleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

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Table 1. Calculated MP2/6-31G* Energies and Heats of Formation[a]

compd	MP2/6-31G*	ΔH_f(MP2)	ΔH_f(model)	strain energy
ketene	−152.147 48	−11.0 (−11.4)		
vinyl alcohol	−153.320 05	−30.8 (−29.8)		
cyclopentene	−194.618 15	+8.0 (+8.1)	+4.1	4.0
cyclopentanone	−269.683 01	−47.2 (−47.2)	−51.3	4.1
cyclohexane	−234.992 43	−29.1 (−29.5)	−29.6	0.1
cyclopentane-1,2-dione	−343.532 06	−65.2	−78.0	12.2
tricyclo[2.1.0.0^{1,3}]pentane (**1**)	−193.285 82	+126.0	−11.2	137.2
tricyclo[3.1.0.0^{1,3}]hexane (**2**)	−232.486 05	+99.3	−16.2	115.5
tricyclo[4.1.0.0^{1,3}]heptane (**3**)	−271.709 91	+57.8	−21.1	79.2
tricyclo[5.1.0.0^{1,3}]octane (**4**)	−310.895 87	+40.0	−26.0	66.0
tricyclo[4.1.0.0^{1,3}]heptan-4-one	−345.574 76	+29.3	−47.8	77.1
tricyclo[4.1.0.0^{1,3}]heptan-4,5-dione	−419.427 00	+8.7	−74.4	83.1
5-methylenetricyclo[4.1.0.0^{1,3}]heptan-4-one	−383.545 18	+4.1	−25.9	74.0
tricyclo[4.1.0.0^{1,3}]hept-4-ene	−270.507 63	+85.9	+7.6	78.3
4-methylenetricyclo[4.1.0.0^{1,3}]heptane	−309.676 84	+78.8	+0.7	78.1
4-methyltricyclo[4.1.0.0^{1,3}]hept-4-ene	−309.680 66	+76.5	+1.2	75.3
4-hydroxytricyclo[4.1.0.0^{1,3}]hept-4-ene	−345.541 67	+43.3	−35.0	78.3
tricyclo[5.1.0.0^{1,3}]octan-5-one	−384.759 07	+12.6	−52.7	65.3
tricyclo[5.1.0.0^{1,3}]octan-4-one	−384.761 89	+10.8	−52.7	63.5
tricyclo[3.1.0.0^{1,3}]hexane-4-ketene	−344.307 38	+101.6	−18.9	120.5
cyclobutylketene	−268.436 42	+12.1	−22.5	34.6

[a] The total energies are given in hartrees (1 H = 627.5 kcal/mol), and the other energies are given in kcal/mol. ΔH_f(MP2) is the heat of formation derived from the MP2 energies. The values in parentheses are the observed energies. The ΔH_f(model) is the unstrained heat of formation estimated using the Franklin group equivalents, and the strain energy is the difference between the MP2 energy and the model energy.

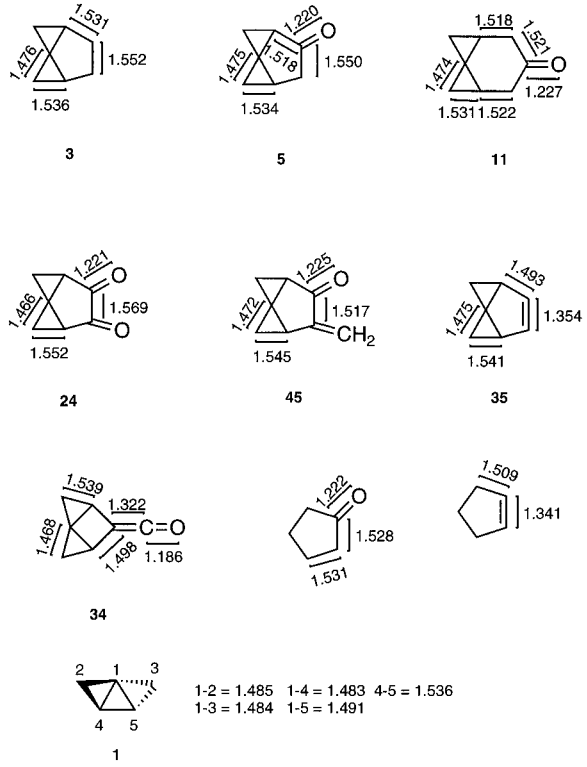


Figure 1. Calculated bond lengths (Å) for compounds optimized at the MP2/6-31G* level of theory.

Hartrees to kcal/mol, E_T is the calculated total energy, n_{CH_3} is the number of CH_3 groups, E_{CH_3} is the corresponding group equivalent, etc. The equivalents include the zero-point energy terms and the change in energy on going from 0 K to 25 °C. Similar schemes have been developed by others.[9]

One might expect that the HF theoretical level would not be adequate for reproducing the relative energies of highly strained compounds. Therefore, we have now obtained a corresponding set of group equivalents based on MP2/6-31G* energies, making use of the calculated energies of a number of small acyclic compounds along with cyclopropane and spiropentane. The values are recorded in Table 2, and the origin of the values is described in the Supporting Information. Making use of these ab initio group equivalents, the heats of formation of the compounds in Table 1 were calculated. Three simple cyclic compounds were included (cyclopentene, cyclopentanone, and cyclohexane) along with ketene and vinyl alcohol as a test of the parameters, and the calculated energies agreed with the experimental values to about the uncertainties in the latter[10] (the observed heats of formation are given in parentheses).[11]

Table 2. Group Energy Terms

a. aliphatic	
CH_3	−39.731 44
CH_2	−39.157 68
CH	−38.583 25
C	−38.009 30
CH_2 (cy-C_3)	−39.156 27
CH (cy-C_3)	−38.581 84
C(spiropentyl)	−38.010 39
b. olefinic	
CH_2	−39.152 48
CH	−38.578 94
C	−38.005 61
c. oxygen containing	
C=O	−112.977 11
OH (secondary)	−75.539 53

Another quantity of interest is the strain energy.[12] Although different schemes give different answers, the values are comparable as long as one scheme is consistently used. We have made use of the Franklin group equivalents[13] to calculate the energies of the correspond-

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

(10) The heats of formation of most of the compounds had an uncertainty of 0.2−0.3 kcal/mol, and that for vinyl alcohol has an uncertainty of 2.0 kcal/mol.

(11) The experimental data were taken from: Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994; Vol. 1.

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

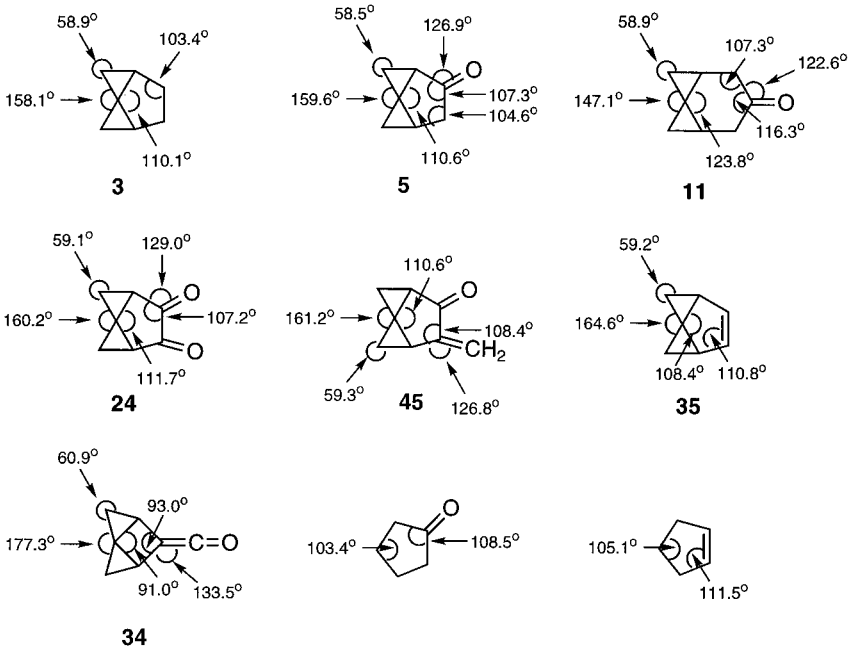


Figure 2. Calculated bond angles (deg) for compounds optimized at the MP2/6-31G* level of theory.

ing unstrained model. The difference between these values and the heats of formation gives the strain energies. The ketene and enol groups are not included in Franklin's table, and we have estimated a value of −7.7 kcal/mol for the C=C=O group and −23.8 for cis-HC=COH.

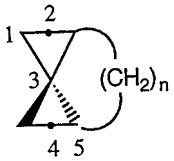
The estimated strain energies of compounds **1**−**4** are 137, 116, 79, and 66 kcal/mol, respectively. As a comparison, the strain energy of spiropentane is 63 kcal/mol. Thus, **4** has essentially the same strain energy as spiropentane. As the bridge becomes smaller, the strain energy increases fairly rapidly.

A comparison of the strain energies in Table 1 illustrates the different factors that affect the total strain in a molecule. Relative to **3**, the introduction of a double bond (**35**) into the bridge leads to a 1 kcal/mol decrease in strain energy, despite the fact that the shorter bridging bond in **35** as compared to **3** leads to a greater distortion of the spiropentyl group in the former (Figures 1 and 2). The lower strain energy in **35** is presumably due to a decrease in the number of hydrogen−hydrogen eclipsing interactions in **3**. Similarly, the introduction of a carbonyl group (**5**) into the bridge results in a 2 kcal/mol decrease in strain relative to **3**. Part of this may result from the stabilizing interaction between the carbonyl group and the cyclopropane ring.[14] In the case of **4**, introduction of a carbonyl group into the 5 position (**11**) reduces the strain energy by 1 kcal/mol as a result in the decrease in eclipsing interactions, and at the 4 position (**10**) the decrease is 2.5 kcal/mol because of the additional interaction between the carbonyl group and the cyclopropane ring.

The structures of the compounds are of some interest (Figures 1 and 2). As noted previously,[5−7] the geometry at the central carbon of **1** is pyramidal, and for **2**, the CH_2-C-CH_2 bond angle is close to 180°. The angle decreases to 158.1° with **3** and to 149.1° with **4**. The introduction of a double bond into the bridge in **3** changes the angle to 164.6° (**35**), and the introduction of a carbonyl group (**5**) changes the angle to 159.6°.

Table 3. Bending and Twisting Distortions

compd	twist	bend
tricyclo[2.1.0.0^{1,3}]pentane (**1**)	21.3°	71.5°
tricyclo[3.1.0.0^{1,3}]hexane (**2**)	6.1°	47.8°
tricyclo[4.1.0.0^{1,3}]heptane (**3**)	6.3°	26.1°
tricyclo[5.1.0.0^{1,3}]octane (**4**)	1.5°	15.0°



Bend = 180° - ∠2,3,4

Twist = 90° - τ1,2,4,5

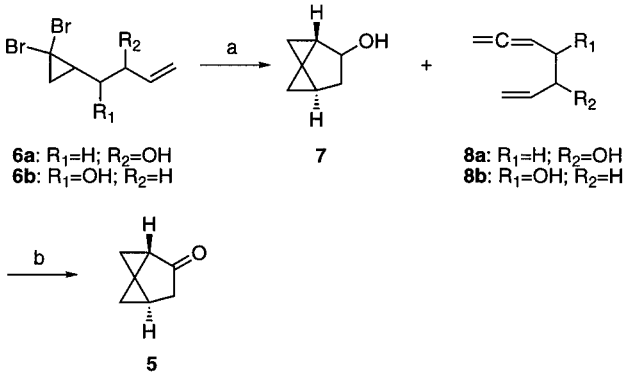
We have discussed the distortion of the spiropentane ring in terms of bending one ring toward the other and of twisting one ring with respect to the other.[5] These angular terms are summarized for **1**−**4** in Table 3.

3. Preparation of Tricyclo[4.1.0.0^{1,3}]heptan-4-one

The key compound for the present study is tricyclo-[4.1.0.0^{1,3}]heptan-4-one (**5**), which has been prepared[15] from 1,5-hexadien-3-ol by addition of dibromocarbene, followed by protection of the hydroxyl group as the trimethylsilyl ether and treatment with methyllithium at −78 °C. The main product was the allene (**8**) formed by cleavage of the intermediate cyclopropylidene. The desired TMS ether was isolated in 7% yield by distillation and preparative gas chromatography. The TMS ether was treated with PCC to give **5** (Scheme 1). It was possible to improve this procedure[16] by eliminating the silation step, and treatment of the crude mixture of **7**, **8a**, and **8b** with ozone destroyed the allenes and oxidized

(13) Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.
(14) Peterson, M. B.; De Mare G. R. *J. Mol. Struct.* **1983**, *104*, 115.
(15) Brinker, U.; Gomann, K.; Zorn, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 869.

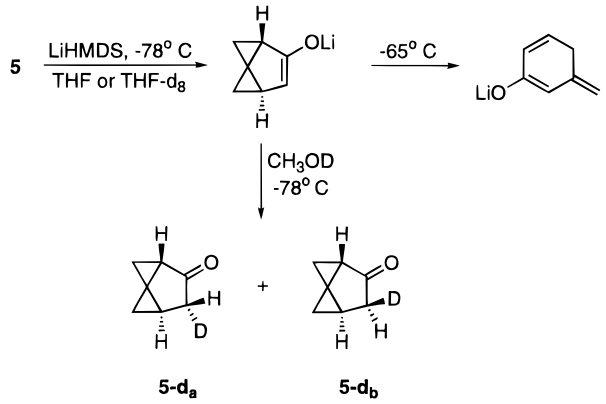
Scheme 1[a]



[a] Conditions: (a) MeLi, Et_2O, −78 °C; (b) (1) O_3, MeOH, −78 °C; (2) Me_2S.

the hydroxyl group of **7** to a carbonyl, thus giving **5** in a 5% yield with a relatively facile workup.

It has been noted that **5** undergoes a fairly facile base-catalyzed rearrangement to *m*-cresol.[15] Treatment of **5** with lithium bis(trimethylsilyl)amide (LHDMS) at −78 °C followed by addition of methanol-*d* at −78 °C gave **5** labeled with deuterium, indicating that the lithium enolate is stable under these conditions. To examine the stability at higher temperatures, a tetrahydrofuran-d_8 solution of **5** was added to a freshly prepared THF-d_8 solution of LHMDS contained in an NMR tube at −78 °C. The tube was inserted into the probe of an NMR spectrometer that had been cooled to −80 °C. The proton NMR spectrum had a band at δ 4.15 ppm corresponding to an enolate proton. The remaining bands were those expected for **5** except for the loss of the ABX pattern for the methylene group α to the carbonyl at 2.4 and 2.6 ppm. No bands downfield from the 4.15 ppm band were observed. The spectrum was unchanged after 1 h at −80 °C.

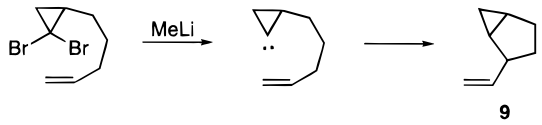


When the probe was warmed to −65 °C, in addition to the bands observed at −80 °C, four bands from 6 to 7 ppm were found. After the probe was warmed to −50 °C, the signal at 4.15 ppm disappeared along with the bands characteristic of the tricyclo[4.1.0.0^{1,3}]heptane ring system. Thus, the enolate ion is stable at low temperature but rearranges readily above −70 °C. Attempts to trap the enolate ion will be described in a later section.

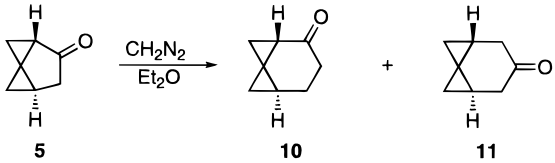
(16) For a preliminary report of this work, see: Wiberg, K. B.; Snoonian, J. R. *Tetrahedron Lett.* **1995**, *36*, 1171.

4. Ring Expansion

An obvious approach to the formation of **4** and its derivatives involves dibromocarbene addition to 1,6-heptadiene followed treatment with methyllithium. This was examined by Skattebøl, who reported the formation of a new compound in small yield.[2] The experiment was repeated by McClusky[6] and by Meibach, Wüster, and Brinker,[17] and the product was shown to be 2-vinylbicyclo[3.1.0]hexane (**9**) rather than the desired tricyclo[5.1.0.0^{1,3}]octane (**4**). Compound **9** was formed by insertion of the carbene into the allylic CH bond instead of addition to the C=C double bond.



An alternate approach to the preparation of three-carbon-bridged spiropentanes was the ring expansion of the ketone, **5**. With strained ketones, diazomethane is often able to effect ring expansion directly.[18] The reaction with **5** proceeded rapidly in ether solution at ambient temperature to give tricyclo[5.1.0.0^{1,3}]octan-4-one (**10**) and -5-one (**11**) in a 20:1 ratio. The compounds were readily separated by chromatography over silica gel and were easily identified by their ^{13}C NMR spectra. Since **10** is asymmetric, it displayed eight bands in its ^{13}C NMR spectrum at δ 13.0 (d), 17.1 (t), 18.6 (t), 22.7 (d), 23.2 (s), 30.6 (t), 38.5 (t), and 212.4 (s) ppm. In contrast, **11** displayed five bands at δ 11.5, 14.3, 15.8, 41.1, and 214.9 ppm in its ^{13}C NMR spectrum because it possesses a C_2 axis of symmetry. The MP2/6-31G* optimized structure of **11** is not C_2 symmetric, but rather the cyclohexanone fragment adopts a twist-boat conformation. It is likely that the three-carbon bridge in **11** has sufficient conformational freedom that an averaged structure is seen on the NMR time scale.



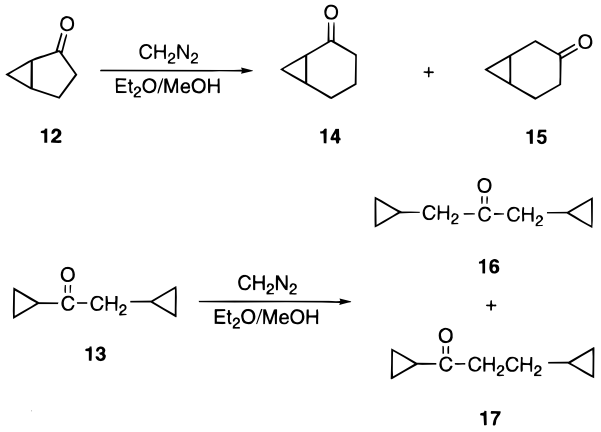
The calculations suggest that **10** has a lower energy than **11** by about 1.8 kcal/mol, which corresponds to a 21:1 ratio at 25 °C. Thus, the observed product ratio (20:1) may be thermodynamically controlled. The rearrangement forming **10** involves the migration of a cyclopropylcarbinyl group, whereas **11** is formed via the migration of a cyclopropyl group. To examine the migratory preference for these groups in less strained compounds, the reactions of both bicyclo[3.1.0]hexan-2-one (**12**) and cyclopropyl cyclopropylcarbinyl ketone (**13**) with diazomethane were studied. Compound **12** corresponds to **5** with the loss of one cyclopropane ring, and compound **13** contains the cyclopropyl and cyclopropylcarbinyl groups found in **5**, but in an acyclic arrangement.

Unlike **5**, neither ketone reacted with diazomethane in ether at an appreciable rate. It is known that

(17) Meibach, T.; Wuster, H.; Brinker, U. H. *J. Org. Chem.* **1993**, *58*, 6520.

(18) For a review, see: Gutsche, C. D. In *Organic Reactions*; John Wiley and Sons: New York, 1954; pp 364−430 and references therein.

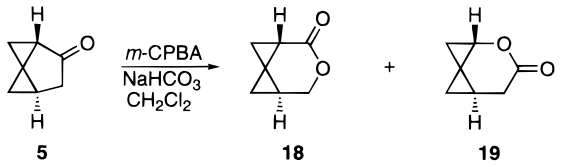
methanol catalyzes the reaction,[18] and therefore **12** and **13** were treated with diazomethane in 1:1 methanol−ether. The reaction of **12** gave bicyclo[4.1.0]heptan-2-(**14**) and -3-one (**15**) in a 3:1 ratio, which was determined by gas chromatography through comparison of the reaction mixture with authentic samples of **14**[19] and **15**.[20] The reaction of **13** led to 1,3-dicyclopropylacetone (**16**)[21] and 1,3-dicyclopropyl-1-propanone (**17**)[21] in a 2:1 ratio. The product ratio **16**:**17** was determined in the same manner used for determination of the ratio of **14**:**15**.



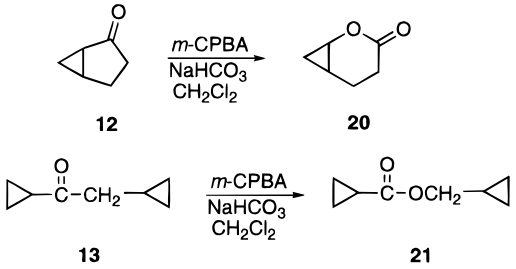
The results clearly indicate that the differences in migratory aptitude in these systems are small. This supports the proposal that the product ratio found with **5** is thermodynamically controlled.

The origin of the difference in reactivity between **5**, **12**, and **13** was also of interest. The relative reactivities were determined by competition, with the ratio of products extrapolated back to zero time. Compound **12** was found to be 3.5 times as reactive as **13**, and **5** was found to be 275 times as reactive. The strain energy decrease on going from **5** to **10** is about 13 kcal/mol (Table 1), whereas with **12**, the strain relief on homologation will be only a few kcal/mol. This factor is more than enough to account for the higher reactivity of **5**.

It was of interest to compare the diazomethane homologation with another ring expansion reaction. One of the more common is the Baeyer−Villiger reaction,[22] which converts cyclic ketones to lactones. Treatment of **5** with *m*-CPBA in dichloromethane buffered with sodium bicarbonate led to two ring-expanded lactones (**18** and **19**) in a 15:1 ratio. The product ratio and the regiochemistry is essentially the same as that observed in the diazomethane reaction.



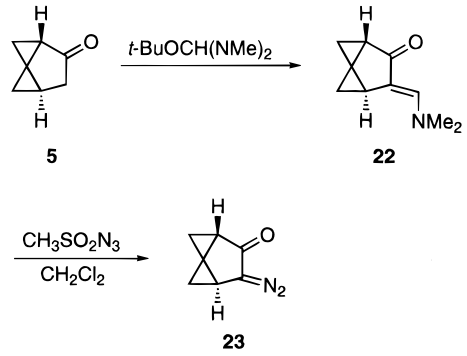
However, this was not the case in the reaction of **12**, which led only to the product (**20**) formed via cyclopropyl migration. When **13** was treated with the peroxyacid, again only one product (**21**) was formed, but here it was the cyclopropylcarbinyl group that migrated. Clearly, there are several factors that control the Baeyer−Villiger reaction, and it is not simply comparable to the diazomethane homologation.



5. Ring Contraction

The simplest approach to the formation of **2** and its derivatives would be the ring contraction of **5**. The photochemical Wolff rearrangement of α-diazo ketones is one of the more general methods for ring contraction.[23] It is known that the reaction is successful for cases where the ring strain increases by 35 kcal/mol or less. The increase in strain on going from **3** to **2** (Table 1) is 37 kcal/mol, at the upper end of the range of applicability.

It is possible to convert the ketone,[24] **5**, to α-enamino ketone **22** in 85% yield via its reaction with Bredereck's reagent.[25] The reaction of **22** with tosyl azide gave only a small yield of the α-diazo ketone **23**. However, the use of methanesulfonyl azide[26] led to a more satisfactory reaction and gave **23** in a 35% yield. The α-diazo ketone was quite stable and could be purified via chromatography over silica gel using 1:1 pentane−ether containing 1.5% triethylamine.



In view of the relatively low yield of **23**, another approach was examined. Treatment of **22** with singlet oxygen led to the diketone **24**, which could be converted to the monotosylhydrazone **25**. The reaction of **25** with base gave **23**. Although each step was satisfactory, the overall yield was not much improved as compared to the diazo group transfer method using methanesulfonyl azide.

(19) Johnson, C. R.; Rogers, P. E. *J. Org. Chem.* **1973**, *38*, 1793.
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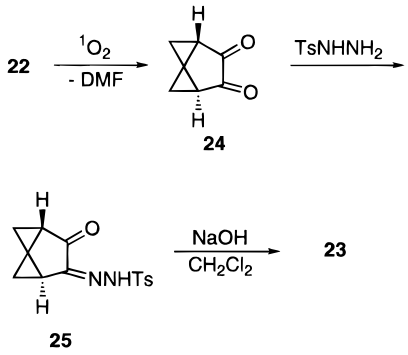
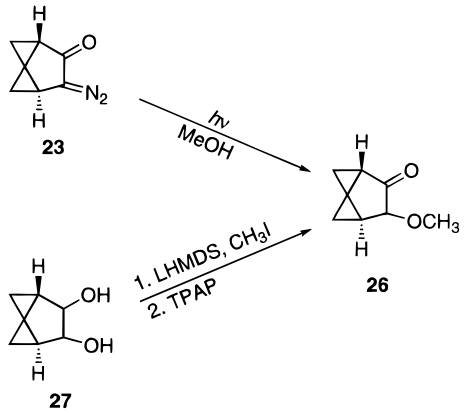
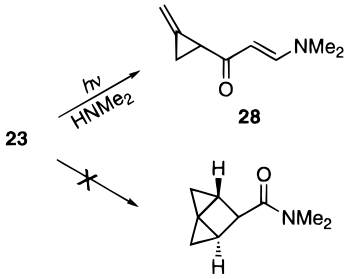
(22) For a review, see: Smith, P. A. S. In *Molecular Rearrangements*; DeMayo, P., Ed.; John Wiley and Sons: New York, 1963; pp 457−592.
(23) For a review, see: Gill, G. B. In *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, 1991; Vol. 3, pp 887−912 and references therein.
(24) For a preliminary report of this work, see: Wiberg, K. B.; Snoonian, J. R.; Lahti, P. M. *Tetrahedron Lett.* **1996**, *37*, 8285.
(25) Bredereck, H.; Simchem, G.; Rebsdat, S.; Kantlehner, W.; Horn, P.; Wahl, R.; Hoffman, H. Grieshaben, P. *Chem. Ber.* **1968**, *101*, 41.
(26) Taber, D. F.; Ruckle, R. E., Jr.; Hennessy, M. *J. Org. Chem.* **1986**, *51*, 4077.



Photolysis of **23** in methanol gave only the methoxy ketone **26**. It was identified by comparison with an authentic sample prepared from the diol **27** by methylation and oxidation with tetrapropylammonium perruthenate (TPAP).[27] The α-diazo ketone is quite stable in methanol, and it is likely that the excited state of **23** is sufficiently basic to abstract a proton from methanol, leading to a diazonium ion that can form **26**. A similar observation was made by Eaton and Temme in their studies leading to a [2.2.2]propellane derivative.[28]

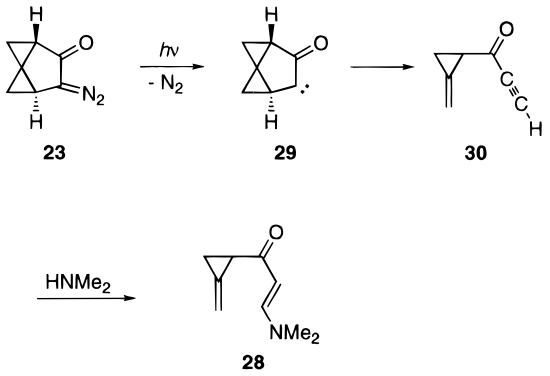


To minimize proton transfer, the photolysis was carried out in dimethylamine at 0 °C. After the excess amine had been allowed to evaporate, the remaining product had a mass (151) corresponding to the loss of nitrogen from **23** and the addition of the elements of dimethylamine. The spectral data for **28** are not compatible with the expected ring-contracted *N*,*N*-dimethylamide. Homonuclear decoupling studies indicated that it had the structure

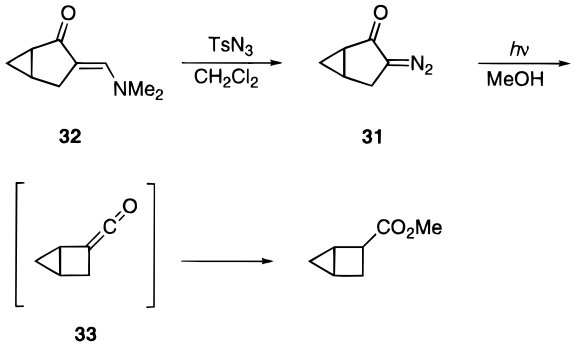


A possible mechanism for the formation of **28** is shown in Scheme 2. Although α-keto carbenes locked into an s-cis conformation are thought to undergo facile rearrangement to ketenes, **29** is not only an α-keto carbene but may be thought of as a cyclopropylcarbene as well. Fragmentation of cyclopropylcarbenes to give alkene and alkyne groups is well known,[29] and would give **30**. Michael addition of dimethylamine to **30** would yield **28**.

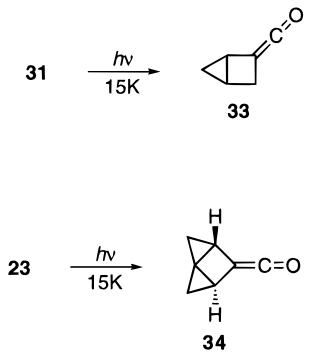
Scheme 2



To gain further information on the photochemistry of **23**, the photolysis was carried out in a Nujol matrix at 15 K using a 1000 W Xenon lamp. As a test of the photolysis, the diazo ketone **31** prepared from **32** was first examined. This diazo ketone undergoes the Wolff rearrangement in methanol to give the expected methyl ester, indicating that the ketene **33** is an intermediate. In the matrix photolysis, the diazo band at 2080 cm^{-1} decreased in intensity and a new band at 2140 cm^{-1} appeared. The latter is at the normal position for a small-ring ketene such as cyclopropylketene.[30]



The photolysis of **23** in a matrix under the same conditions led to the same result: a decrease in the diazo band at 2085 cm^{-1} with the formation of a new band at 2117 cm^{-1}.



(27) Griffith, W.; Ley, S. V.; Whitcombe, G. P.; White, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1625.

(28) Eaton, P. E.; Temme, G. H. *J. Am. Chem. Soc.* **1973**, *95*, 7508.

(29) Cristol, S. J.; Harrington, J. K. *J. Org. Chem.* **1963**, *28*, 1413.

Table 4. Scaled Infrared Frequencies and Corresponding Intensities for 34 Calculated at the HF/6-31G* Level of Theory[a] (Frequencies Are in cm^{-1})

frequency	intensity	frequency	intensity
90	0.2	1081	2.2
154	2.4	1088	6.2
294	2.1	1092	1.8
353	4.2	1120	3.6
455	4.6	1124	8.6
498	0.4	1246	12.4
523	34.0	1262	17.6
605	17.5	1403	0.0
630	13.3	1406	0.7
748	0.6	1453	0.3
758	0.3	1495	9.1
878	10.0	**2109**	**1460**
880	18.9	2943	53.0
896	0.2	2943	15.4
956	14.5	2991	2.9
986	0.8	2991	39.2
1013	17.9	3018	31.5
1034	0.1	3018	4.2

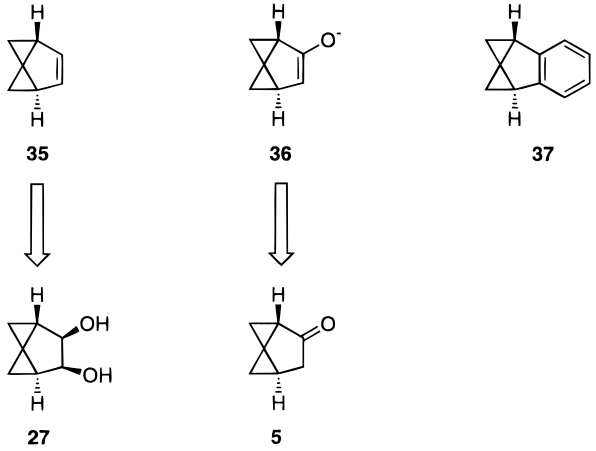
[a] The scaling factor was 0.893.

The calculated frequencies for **34** are given in Table 4. No imaginary frequencies were calculated for **34** at the HF/6-31G* level of theory. An intense band calculated at 2362 cm^{-1} corresponds to the experimentally observed intense ketene stretch at 2117 cm^{-1}. When the calculated values are scaled by a factor of 0.893, the frequency of this intense band was found to be 2109 cm^{-1}, which is in excellent agreement with the experimentally observed value of 2117 cm^{-1}. A scaling factor of 0.893 is often used to correct for anharmonicity and other effects when frequencies are calculated at the HF/6-31G* level of theory.[31] Thus, it appears that under matrix isolation conditions **23** does undergo the normal Wolff rearrangement.

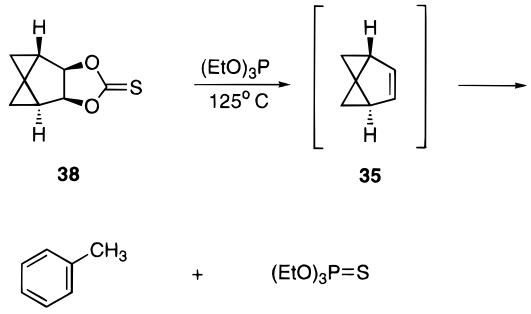
6. Tricyclo[4.1.0.0^{1,3}]hept-4-ene Derivatives

Tricyclo[4.1.0.0^{1,3}]hept-4-ene (**35**) has not been reported, and in view of the thermal instability of the enolate ion **36** it is likely that it would not be stable at room temperature. The alkene was of interest in that the distortion in the spiropentane unit would be increased as a result of decreasing the bridging C−C bond length. However, the calculations (Table 1) suggest that the strain energy for **35** would be less than that of **3**, presumably due to loss of some eclipsing interactions. It should be noted that **37** has been prepared and is quite stable.[32] However, here the opportunities for rearrangement are minimized.

Two approaches were taken for the attempted preparation of **35** by deoxygenation of the vicinal diol **27**. The synthesis and additional studies of **27** and thiocarbonate **38** are reported elsewhere.[33] Corey and Winter have shown that thiocarbonate esters may be converted to alkenes using trialkyl phosphites.[34] The reaction of **38** with triethyl phosphite was remarkably slow, and



essentially no reaction occurred under 100 °C. Desulfurization was complete on heating at 125 °C for 6 h, and the products were toluene and triethyl thiophosphate. It seems likely that **35** was formed and rearranged to toluene under the reaction conditions.



Some highly strained alkenes, such as *trans*-cycloheptene, have been formed and trapped by 1,3-diphenylisobenzofuran in situ.[35] This reaction was carried out with **38**, and besides triethyl thiophosphate and excess 1,3-diphenylisobenzofuran, analysis by GC/MS indicated there was a product having two main fragments at 271 and 91. The desired adduct would have a mass of 362, the sum of the observed masses. However, it was not the adduct with **35** since the NMR spectrum did not contain any bands characteristic of cyclopropane rings.

Another elimination reaction that usually occurs at a lower temperature is the cleavage of the anion derived from a 2-phenyl-1,3-dioxolane derivative.[36] The requisite benzylidene acetal was formed by treatment of the diol, **27**, with benzaldehyde dimethyl acetal and a catalytic amount of *p*-toluenesulfonic acid. The NMR spectrum indicated that the two epimeric dioxolanes (**39a**) and (**39b**) were formed in approximately equal amounts, and it was possible to separate the epimers by silica gel column chromatography. When a petroleum ether solution of **39a** and **39b** was treated with 2 equiv of *n*-butyllithium in hexane, the color slowly changed from colorless to orange. After 3 h, the solution was treated with D_2O, which discharged the orange color. The starting materials were the only products isolated, but they now contained one deuterium. When the reaction solution was allowed to stand for 30 h before workup, the products were toluene and valerophenone.

(30) Maquestiau, A.; Pauwels, P.; Flammang, R.; Lorencak, P.; Wentrup, C. *Org. Mass. Spectrom.* **1986**, *21*, 259. Maier, G.; Heider, M.; Sierakowski, C. *Tetrahedron Lett.* **1991**, *32*, 1961.

(31) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622. Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

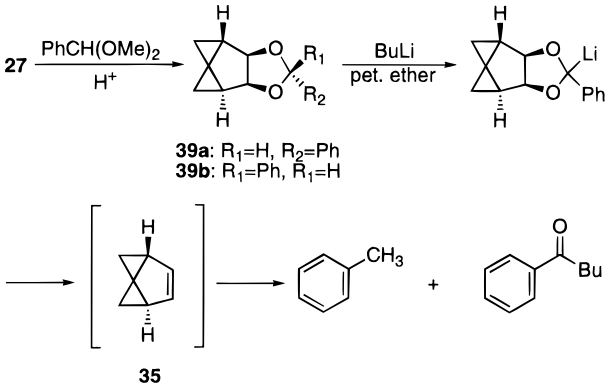
(32) Brinker, U.; Streu, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 631.

(33) Wiberg, K. B.; Snoonian, J. R. *J. Org. Chem.* **1998**, *63*, 1402.

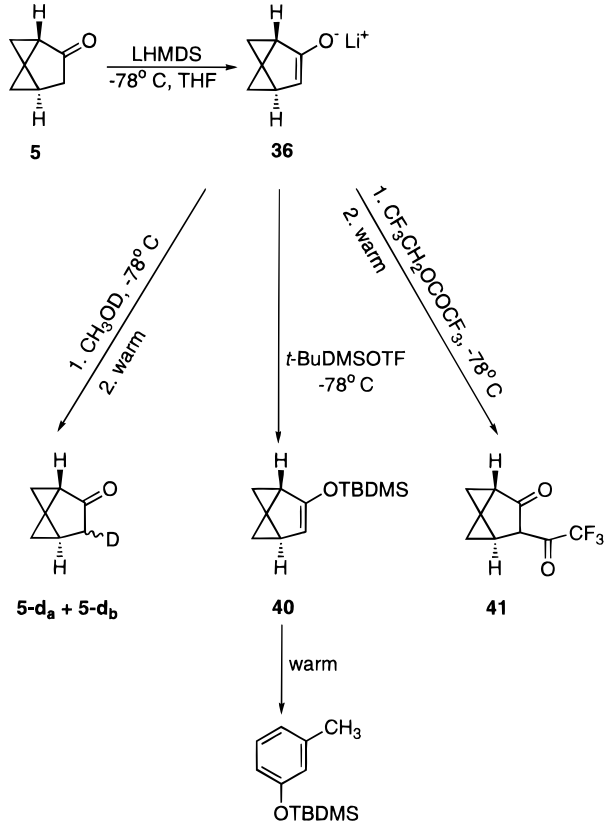
(34) Corey, E. J.; Winter, R. A. E. *J. Am. Chem. Soc.* **1963**, *85*, 2677.

(35) Corey, E. J.; Winter, R. A. E. *J. Am. Chem. Soc.* **1965**, *87*, 934.

(36) Wharton, P. S.; Hiegel, G. A.; Ramaswami, S. *J. Org. Chem.* **1964**, *29*, 2441.



Given the ease with which **35** rearranges to toluene, our efforts were now directed toward the trapping of the enolate ion **36** and observing whether the compound thus formed would survive warming to room temperature. Since we have determined that **36** is stable at −78 °C, a THF solution of **36** at −78 °C was treated with *tert*-butyldimethylsilyl triflate, which normally reacts at the oxygen of an enolate. On warming to room temperature, the product was found to be the silyl ether of *m*-cresol, indicating that the enol ether **40** underwent rearrangement below room temperature.

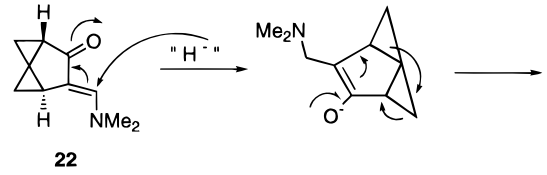


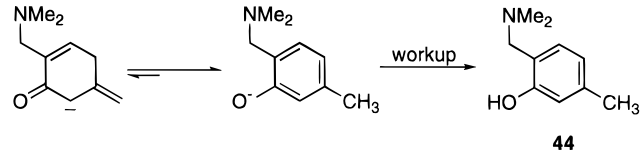
When **36** at −78 °C was treated with 2,2,2-trifluoroethyl trifluoroacetate, which normally gives C acylation, followed by aqueous workup, the NMR spectrum showed no aromatic or olefinic protons. The EI mass spectrum showed a parent peak at 204, along with an intense peak at 135 corresponding to the loss of the trifluoromethyl group. The compound **41** was quite unstable, and attempts to purify it were unsuccessful.

7. Discussion

This work has led to the preparation of the first-known derivatives of **4** via the homologation of **5** with diazomethane. Although the cyclopropylcarbinyl group migrated in preference to cyclopropyl in this reaction, an examination of related ketones found little preference between these groups. Thus, it appears that the migratory preference is determined largely by the difference in energy between the two ketones that are formed. The high reactivity of **5** toward diazomethane also appears to be derived from thermochemical factors.

The Corey-Winter reaction of **38** and the base-induced elimination of lithium benzoate from **39a** and **39b** yielded toluene by rearrangement of **35**. The facile rearrangement of **35** to toluene is supported by the NMR studies of **36**, which showed that it rearranges at −65 °C. A similar mechanism can be written for the reaction of **22** with lithium aluminum hydride, in which the benzene derivative **44** was produced in 72% yield.





Matrix photolysis of **23** produced a band in the IR at 2117 cm^{-1} attributed to ketene **34**, which indicates that for the first time a derivative of the tricyclo[3.1.0.$0^{1,3}$]-hexane ring system **2** has been prepared. The apparent dichotomy in the behavior of **23** between solution and low-temperature matrix photolysis is interesting and will receive further study. One of several possibilities is that the ketocarbene **29** forms an ylide with dimethylamine and this ylide, not ketocarbene **29**, undergoes rearrangement leading to **28**. It is known that carbenes react with amines such as pyridine to form relatively stable ylides,[37] and studies directed toward the detection and measurement of the lifetime of **29** are in progress.

Finally, a group-equivalent scheme was developed that has shown good agreement with experimental thermochemical data and has been useful in the interpretation of our experimental observations. This scheme should be of use to others that wish to convert total energies calculated at the MP2/6-31G* level of theory to heats of formation at 298 K.

8. Experimental Section

General Information. All reactions were conducted in oven-dried or flame-dried glassware under an argon atmosphere. Reagents were purchased from Aldrich, Fisher, J. T. Baker, or Lancaster Chemical Co. and were used without further purification unless otherwise stated. Air-sensitive solutions were transferred via oven-dried syringe needles or

(37) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 8985. Wang, J. L.; Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477.

an oven-dried cannula under positive pressure of argon. Concentration in vacuo refers to removal of volatiles on a rotary evaporator at water aspirator pressure. FT NMR spectra were taken in $CDCl_3$. Proton spectra were recorded at 300 MHz, and ^{13}C NMR were recorded at 75 MHz. In both cases, residual $CHCl_3$ served as the internal standard with proton spectra referenced to δ 7.26 ppm and carbon spectra referenced to δ 77.0 ppm (center of triplet). In ozonolyses reactions, the ozone was generated by passing oxygen through an OREC V-10 ozone generator. Low-resolution mass spectra obtained in the EI mode by GC/MS were obtained at an ionizing voltage of 70 eV using a gas chromatograph fitted with a 30 m × 0.25 mm i.d. capillary column coated with a 0.25 μm layer of SE-30. Mass spectra obtained in the CI mode were obtained using isobutane as the reagent gas. Where mass spectral data are given, the peak value is immediately followed by its relative abundance in parentheses. FT IR spectra were taken in CCl_4 using an NaCl solution cell. Silica gel column chromatography was performed using 230−400 mesh silica gel. TLC analyses were done on glass plates coated with 250 μm of silica gel. Plates were visualized with vanillin stain, UV light, or iodine vapor. In cases where a product was purified by silica gel column chromatography, the R_f value given is that of the compound using the eluant employed for purification unless otherwise stated. Boiling and melting points are uncorrected. Combustion analyses were performed by Atlantic Microlab, Norcross, GA. High-resolution mass spectra were obtained at the University of Illinois Urbana−Champaign. Unless otherwise stated, HRMS data was obtained in the EI mode. All calculations were performed using the developmental version of GAUSSIAN 95.[38] Unless otherwise stated, all of the calculated energy values and geometrical parameters were obtained by using the FOPT option at the MP2[39] level of theory, the 6-31G* basis set,[40] and the frozen core approximation.[41] *Although no difficulties were encountered using p-toluenesulfonyl azide, methanesulfonyl azide, and diazomethane, due to their explosive nature these reagents should be handled with care behind a safety shield.*

1,1-Dibromo-2-(2-hydroxy-3-butenyl)cyclopropane (6a) and 1,1-Dibromo-2-(1-hydroxy-3-butenyl)cyclopropane (6b). To a solution of 73 g (0.75 mol) of 1,5-hexadien-3-ol, 289 g (1.14 mol) of bromoform, and 6.7 g (29 mmol) of benzytriethylammonium chloride in 150 mL of CH_2Cl_2 was added dropwise with vigorous stirring 135 g of NaOH in 270 mL of water over 30 min. The solution refluxed strongly and became deep brown and viscous. After vigorous stirring for 36 h, 1 L of cold water was added. The layers were separated, and the aqueous layer was extracted with 300 mL of CH_2Cl_2. The total organic phase was washed with two 300 mL portions of 0.1 N HCl, dried over Na_2SO_4, and concentrated in vacuo. The tarry, brown residue was vacuum distilled (bp 85−95 °C, 0.15 Torr) using a 15 cm × 1.5 cm Vigreux column to give a 62.0 g (31% yield) mixture of the regioisomeric dibromides: ^1H NMR δ 1.21−2.79 (10H, m), 3.48−3.54 (1H, m), 4.30−4.41 (1H, m), 5.14−5.37 (4H, m), 5.82−6.01 (2H, m); CIMS 255 (20), 253 (40) = [(M + H)] − 18, 251 (21), 173 (45), 171 (42), 91 (100).

Tricyclo[4.1.0.0^{1,3}]heptan-4-one (5). To 220 mL of 1.4 M MeLi (salt free, diethyl ether solution) at −78 °C was added dropwise a 35.0 g (0.13 mol) mixture of **6a** and **6b** in 450 mL of Et_2O over 6 h. After the addition was complete, the solution was stirred at −78 °C for an additional hour and then allowed to warm to 0 °C. Excess MeLi was decomposed through careful addition of water. The quenched solution was washed with two 200 mL portions of saturated NH_4Cl, dried over Na_2SO_4, and concentrated in vacuo. Approximately 14 g of a yellow liquid remained. This mixture of **7**, **8a**, and **8b** was dissolved in 75 mL of absolute MeOH and treated with O_3 at −78 °C until an opaque-blue-white color persisted. After the solution was purged of excess O_3, 50 mL of Me_2S was added at −78 °C. The solution was allowed to warm to room temperature and then concentrated in vacuo. The concentrate was poured into water, and this aqueous layer was repeatedly extracted with pentane until TLC (Et_2O, R_f = 0.8) revealed that no more ketone remained in the aqueous layer. The pentane extracts were combined, dried over Na_2SO_4, and concentrated in vacuo. Silica gel column chromatography using 3:1 pentane:Et_2O as the eluant typically gave 0.8 g of 5 (6% yield) (R_f = 0.55).

5: IR 1721 cm^{-1}; ^1H NMR δ 0.98−1.01 (1H, m), 1.57−1.61 (1H, m), 1.69−1.73 (1H, m), 1.98−2.02 (1H, t), 2.16−2.18 (1H, m), 2.18−2.24 (1H, m), 2.43, 2.64 (2H, ABX); ^{13}C NMR δ 11.56, 20.80, 22.65, 29.67, 30.25, 46.20, 216.59; GC/MS 108 (50), 107 (21), 79 (96), 39 (100).

Tricyclo[5.1.0.0^{1,3}]octan-4-one (10) and Tricyclo[5.1.0.0^{1,3}]-octan-5-one (11). Diazomethane was formed from 2.5 g (11.7 mmol) of Diazald using the procedure described by the Aldrich Chemical Co.[42] and added to 0.550 g (5.1 mmol) of **5** (neat) so as to react in situ with the diazomethane. After being stirred for 18 h at room temperature, the solution was cooled in an ice bath, and excess CH_2N_2 was decomposed through careful addition of an ethereal solution of acetic acid. The solution was concentrated in vacuo, and the yellow residue was purified by silica gel column chromatography using 2:1 CH_2Cl_2:pentane as the eluant. This gave 0.435 g of pure **10** (R_f = 0.19). A second, less polar fraction with an R_f = 0.50 containing **5** and **11** was inseparable by various column chromatographic conditions. These two compounds were separated by preparative gas chromatography using a 13% OV101 on AWDMS column at 165 °C. Approximately 20 mg of **11** was obtained.

10: IR 1700 cm^{-1}; ^1H NMR δ 1.11−1.20 (2H, m), 1.24−1.36 (1H, m), 1.51−1.55 (1H, q), 1.59−1.61 (1H, t), 1.68−1.77 (2H, m), 2.05−2.11 (2H, m), 2.31−2.37 (1H, m); ^{13}C NMR δ 13.04 (d), 17.09 (t), 18.57 (t), 22.68 (d), 23.17 (s), 30.60 (t), 38.52 (t), 212.41 (s); GC/MS 122 (8), 94 (12), 79 (100); CIMS 123 (100); HRMS calcd for $C_8H_{10}O$ 122.0732, found 122.0730.

11: IR 1714 cm^{-1}; ^1H NMR δ 0.83 (2H, s, broad), 1.38−1.59 (4H, m), 1.85−1.94 (2H, d of d), 2.55−2.63 (2H, d of d); ^{13}C NMR δ 11.49, 14.30, 15.82, 41.05, 214.92. MS (EI): 122 (7), 79 (100); CIMS 123 (100); HRMS calcd for $C_8H_{10}O$ 122.0732, found 122.0730.

5-Oxatricyclo[5.1.0.0^{1,3}]octan-4-one (18) and 4-Oxatricyclo[5.1.0.0^{1,3}]octan-5-one (19). To a mixture of 0.70 g (4.1 mmol) of *m*-CPBA and 1.3 g (15.5 mmol) of $NaHCO_3$ in 10 mL of CH_2Cl_2 was added 0.25 g (2.3 mmol) of **5** in 2 mL of CH_2Cl_2. After being stirred for 18 h, the mixture was washed with 5 mL of 10% Na_2SO_3 and then 5 mL of saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The lactones were purified by silica gel column chromatography using 3:1 Et_2O:pentane as the eluant, and 0.013 g of **19** eluted first (R_f = 0.61). The major product was **18** (R_f = 0.30), and 0.150 g was isolated. Recovered starting material accounted for the remaining material.

18: IR 1746 cm^{-1}; ^1H NMR δ 1.31−1.39 (1H, t),1.42−1.50 (2H, m) 1.63−1.67 (1H, t), 1.69−1.82 (ABX, 2H), 3.72−3.79 (1H, d of d), 4.62−4.69 (1H, d of d); ^{13}C NMR δ 11.29, 12.86, 15.35, 16.73, 18.22, 75.64, 171.89; GC/MS 124 (2), 95 (18), 79 (100), 67 (41), 39 (52); CIMS 125 (100). Anal. Calcd for $C_7H_8O_2$: C, 67.7; H, 6.5. Found: C, 67.6; H, 6.4.

19: IR 1763, 1751 cm^{-1}; ^{13}C NMR δ 11.14, 12.04, 14.62, 16.01, 33.39, 56.91, 173.48; GC/MS 95 (96), 67 (100), 53 (54), 41 (57), 39 (79); CIMS 125 (100).

Reaction of the Ketone 12 with *m*-CPBA. To a mixture of 3.6 g (20.9 mmol) of *m*-CPBA and 7.0 g (83.3 mmol) of $NaHCO_3$ in 50 mL of CH_2Cl_2 was added 1.1 g (10.4 mmol) of

(38) Gaussian 95, Development Version (Revision D.2): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Strain, M. C.; Burant, J. C.; Stratman, E.; Petersson, G. A.; Montgomery, J. A.; Zakrzewski, V. G.; Keith, T.; Raghavachari, K.; Al-Laham, M. A.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Gonzalez, C.; Head-Gordon, M.; Gill, P. M. W.; Johnson, B. G.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1996.

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12. After being stirred for 48 h, the mixture was washed with two 100 mL portions of 10% Na_2SO_3 and then 200 mL of saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The product was purified by silica gel column chromatography using 1:1 Et_2O:pentane as the eluant. The reaction was extremely slow, and only 0.115 g of **20** (R_f = 0.37) was isolated. Recovered starting material accounted for the remaining material.

20: ^{1}H NMR δ 0.79−0.84 (1H, t of d), 0.92−0.99 (1H, m), 1.28−1.32 (1H, m), 1.81−1.84 (1H, m), 2.30−2.48 (3H, m), 4.05−4.10 (1H, t of d); ^{13}C NMR δ 9.32 (d), 12.63 (t), 21.19 (t), 28.27 (t), 55.42 (d), 171 (s); GC/MS 84 (100), 55 (55), 42 (50); CIMS 113 (100); HRMS calcd for $C_6H_8O_2$ 112.0524, found 112.0524.

Reaction of the Ketone 13 with *m*-CPBA. To 2.8 g (16.1 mmol) of *m*-CPBA and 5.4 g (64.3 mmol) of $NaHCO_3$ in 40 mL of CH_2Cl_2 was added 1.0 g (8.2 mmol) of **13** in 8 mL of CH_2Cl_2. After being stirred for 48 h, the mixture was washed with 20 mL of 10% Na_2SO_3 and then 20 mL of saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Silica gel column chromatography using 3:1 pentane:CH_2Cl_2 as the eluant gave 0.083 g of **21** (R_f = 0.31). The reaction was extremely slow, and recovered starting material accounted for the remaining material.

21: IR 1728 cm^{-1}; ^{1}H NMR δ 0.23−0.28 (2H, q), 0.52−0.58 (2H, m), 0.80−0.89 (2H, m), 0.95−1.05 (2H, m), 1.08−1.16 (1H, m), 1.57−1.65 (1H, m), 3.87−3.89 (2H, d); ^{13}C NMR δ 3.11, 8.25, 9.84, 12.88, 69.13, 174.90; GC/MS 69 (100), 39 (24); CIMS 141 (100). Anal. Calcd for $C_8H_{12}O_2$: C, 68.6; H, 8.6. Found: C, 68.4; H, 8.6.

Reaction of Ketone 12 with Diazomethane. Diazomethane was formed from 3.5 g (16.4 mmol) of Diazald using the procedure described by the Aldrich Chemical Co.[42] and added to 1.0 g (10.4 mmol) of **12** in 10 mL of absolute MeOH. After the mixture was stirred at room temperature for 36 h, the flask was cooled in an ice bath and excess diazomethane was decomposed through careful addition of an ethereal solution of acetic acid. Product analysis by GC and GC/MS showed that bicyclo[4.1.0]heptan-2-one (**14**) and bicyclo[4.1.0]-heptan-3-one (**15**) were present in a 3:1 ratio, respectively.

Reaction of the Ketone 13 with Diazomethane. Diazomethane was formed from 2.5 g (11.7 mmol) of Diazald using the procedure described by the Aldrich Chemical Co.[42] and added to 0.50 g (4.03 mmol) of **13** in 4 mL of absolute MeOH. After the mixture was stirred at room temperature for 36 h, the flask was cooled in an ice bath, and excess diazomethane was decomposed through careful addition of an ethereal solution of acetic acid. Product analysis by GC and GC/MS showed that 1,3-dicyclopropyl-2-propanone (**16**) and 1,3-dicyclopropyl-1-propanone (**17**) were present in a 2:1 ratio, respectively.

Relative Rate Constants for Reaction of the Ketones 5, 12, and 13 with Diazomethane. General procedure. To an ethereal solution of diazomethane cooled in an ice bath was added a mixture of two ketones dissolved in absolute MeOH. Aliquots were removed at regular time intervals, immediately transferred to test tubes that had been precooled in ice, and quenched by addition of an ethereal solution of acetic acid. Product analyses were determined by GC through comparison with the retention times of authentic samples. Typically, an excess of the less reactive ketone was used in order to detect its respective products. The product ratios were corrected to account for this and were plotted as a function of reaction time. The product ratio was extrapolated to time zero, thus giving the relative rate constants.

A. 12 vs 13. A solution of 0.284 g (2.29 mmol) of **13** and 0.105 g (0.96 mmol) of **12** in 15.0 mL of absolute MeOH was added to an excess of diazomethane (9.2 mmol). Aliquots were removed and quenched 5, 10, 15, 20, 30, 45, and 60 min following the start of the reaction.

B. 12 vs 5. A solution of 0.900 g (9.34 mmol) of **12** and 0.011 g (0.10 mmol) of **5** in 2.0 mL of absolute MeOH was added to an excess of diazomethane (20 mmol). Aliquots were removed 1, 2, 3, 4, 5, and 10 min following the start of the reaction.

5-[(*N*,*N*-Dimethylamino)methylene]tricyclo[4.1.0.0^{1,3}]-heptan-4-one (22). To 1.07 g (9.9 mmol) of the ketone **5** was added 2.86 g (16.4 mmol) of *tert*-butoxybis(dimethylamino)-methane dropwise over 45 min. The mixture was stirred under argon at room temperature for 36 h. The mixture was transferred to a 100 mL flask with the aid of Et_2O. The Et_2O was removed in vacuo, and the excess *tert*-butoxybis(dimethylamino)methane was removed under high vacuum (1.5−2.0 Torr) at room temperature. Silica gel column chromatography of the viscous, maroon residue using 85:15 Et_2O:MeOH (R_f = 0.82) as the eluant gave 1.37 g of **22** as a deep red-orange oil.

22: IR 1686, 1597 cm^{-1}; ^{1}H NMR δ 1.50−1.54 (m, 2H), 1.64−1.68 (t, 1H), 1.79−1.84 (m, 2H), 1.98−2.01 (d of d, 1H), 3.11 (s, 6H), 7.03 (s, 1H); ^{13}C NMR δ 18.31 (d), 19.87 (t), 19.99 (t), 22.94 (s), 29.84 (d), 109.48 (s), 146.69 (d), 204.56 (s), the nitrogen methyl groups were not observed even using a pulse-delay of 10 s; GC/MS 163 (100), 120 (59), 108 (50), 94 (43), 81 (55), 42 (89); CIMS 164 (100); HRMS calcd for $C_{10}H_{13}NO$ 163.0998, found 163.0997.

5-Diazotricyclo[4.1.0.0^{1,3}]heptan-4-one (23). To 1.37 g (8.40 mmol) of **22** in 50 mL of CH_2Cl_2 was added 1.70 g (14.1 mmol) of methanesulfonyl azide in one portion. The flask was kept in the dark, and the progress of the reaction was monitored by TLC (85:15 Et_2O:MeOH). After the mixture was stirred for 72 h under argon, no starting material could be detected, and to the deep red solution was added 150 mL of CH_2Cl_2. The organic solution was washed with three 50 mL portions of 10% aqueous NaOH. The combined aqueous washings were extracted with 50 mL of CH_2Cl_2, and then the total organic layer was dried over Na_2SO_4. The CH_2Cl_2 was removed in vacuo, and silica gel column chromatography of the remaining red, viscous oil using 1:1 pentane:Et_2O containing 1.5% Et_3N by volume afforded 0.327 g of **23** as a deep orange-red oil.

23: IR 2080, 1687 cm^{-1}; ^{1}H NMR δ 1.65−1.69 (d of d, 1H), 1.81−1.86 (t of d, 1H), 1.98−2.09 (m, 3H), 2.10−2.14 (d of d, 1H); ^{13}C NMR δ 14.97, 18.86, 19.03, 22.12, 29.43, 65.69, 199.20; CIMS 135 (24), 107 (21), 79 (100).

Attempted Wolff Rearrangement of the Diazo Ketone 23 in Methanol. A solution of 0.050 g (0.37 mmol) of **23** in 7 mL of absolute MeOH was purged with argon, immersed in an ice−water bath, and irradiated for 1 h with a 450 W medium-pressure mercury arc lamp. Thin-layer chromatography (1:1 pentane:Et_2O) indicated that **23** had been consumed. Many spots were present, and the solution contained a tan polymeric mass. Proton NMR analysis of the mixture did not support the presence of the desired ring-contracted product. The only product isolated from this reaction was 5-methoxytricyclo[4.1.0.0^{1,3}]heptan-4-one (**26**).

26: IR 1747 cm^{-1}; ^{1}H NMR δ 1.05−1.09 (1H, q), 1.16−1.20 (1H, m), 1.44−1.46 (1H, t), 1.69−1.73 (2H, d), 1.86−1.90 (1H, t), 3.31 (3H, s), 3.41 (3H, s), 4.05−4.08 (1H, t); GC/MS 138 (5), 107 (99), 79 (100), 67 (60), 39 (94).

5-Methoxytricyclo[4.1.0.0^{1,3}]heptan-4-one (26). To 5.7 mL of a 1.0 M THF solution of NaHMDS cooled in ice−water was added 0.355 g (2.82 mmol) of **27** in 28 mL of THF dropwise over 2.5 h. The solution was stirred for 30 min, and then 0.40 g (2.82 mmol) of CH_3I in 7 mL of THF was added dropwise over 1 h. The solution was stirred at room temperature for 24 h and then poured into 50 mL of Et_2O and 50 mL of water. The aqueous layer was extracted with two 40 mL portions of Et_2O. The total organic layer was washed with 40 mL of saturated NH_4Cl, dried over Na_2SO_4, and concentrated in vacuo. Silica gel column chromatography of the pink residue afforded 0.224 g of the monomethyl ether of **27** (R_f = 0.8). To 0.125 g (0.893 mmol) of the monomethyl ether of **27** and 0.167 g (1.427 mmol) of *N*-methylmorpholine *N*-oxide in 9 mL of CH_2Cl_2 was added two spatulafuls of 4 Å molecular sieves. Then 0.015 g (0.045 mmol) of TPAP was added in one portion. After 18 h, the solution was diluted to 50 mL with additional CH_2Cl_2 and then washed with 15 mL of saturated Na_2SO_3, 15 mL of saturated NaCl, and 15 mL of saturated $CuSO_4$. The solution was dried over Na_2SO_4 and concentrated in vacuo. Silica gel column chromatography using 2:1 pentane:Et_2O as the eluant gave 0.054 g of **26** (R_f = 0.27). Spectral data for

this sample were identical to that obtained from photolysis of **23** in methanol.

Attempted Wolff Rearrangement of 23 in Dimethylamine. To 0.050 g (0.37 mmol) of **23** in a Pyrex tube cooled in an ice−water bath was added 7 mL of dimethylamine with the aid of a coldfinger. The mixture remained immersed in the ice−water bath and fitted with the coldfinger while being irradiated with a 450 W medium-pressure mercury arc lamp. Once TLC (1:1 pentane:Et_2O) had indicated **23** had been consumed, the dimethylamine was allowed to evaporate at room temperature. The product was purified by silica gel column chromatography using 3:1 Et_2O:pentane as the eluant (R_f = 0.23). The product was determined to be 2-(*N*,*N*-dimethylamino)vinyl 2-methylenecyclopropyl ketone, **28**, via the decoupling experiments described in the Supporting Information.

28: IR 1658, 1620, 1579 cm^{-1}; ^1H NMR δ 1.51−1.59 (1H, t of t), 1.77−1.83 (1H, m), 2.40−2.46 (1H, m), 2.83 (NCH_3, broad), 3.05 (NCH_3, broad), 5.03−5.07 (1H, d, J = 12.6 Hz), 5.41−5.49 (2H, d of t) 7.56−7.60 (1H, d, J = 12.6 Hz); ^{13}C NMR δ 11.7 (t), 25.7 (d), 94.1 (d), 103.2 (t), 133.7 (s), 152.5 (d), 194.5 (s); CIMS 152 = M + 1, (100).

Attempted Synthesis of the Alkene 35 by Corey−Winter Reaction of 38. A solution of 0.100 g (0.595 mmol) of **38** in 2 mL of triethyl phosphite was heated to reflux using a 125 °C oil bath. The progress of the reaction was monitored by TLC (Et_2O) and was complete after stirring for 5 h at 125 °C as evidenced by the consumption of the thiocarbonate (R_f = 0.77). A small amount of the cooled reaction mixture was dissolved in CH_2Cl_2, and analysis by GC/MS found only $(EtO)_3P$ and $(EtO)_3P{=}S$. Analysis by GC showed that a third peak was present and was determined to be toluene by comparison with authentic toluene. The toluene was not detected by GC/MS because it eluted during the initial 3 min solvent delay.

Attempted Synthesis of the Alkene 35 by Reaction of 39a and 39b with *n*-Butyllithium. To 0.185 g (0.864 mmol) of the acetals **39a** and **39b** in 4 mL of petroleum ether (bp 35−65 °C) was added 1.1 mL of a 1.6 M hexane solution of *n*-BuLi (1.73 mmol) dropwise over 30 min. The reaction progress was monitored by TLC (4:1 pentane:Et_2O). After 1 h, only the starting material was detected, and after 3 h, the solution was now orange, but again only starting material was present. A small aliquot of this orange solution was removed and quenched with D_2O (99.8% atom-d). This sample was dried, and analysis by GC/MS showed that in addition to small baseline peaks **39a** and **39b** were still present, but their mass had increased by 1. After 30 h, the deep orange solution was quenched with 2 mL of water and added to 20 mL of Et_2O and 10 mL of water. The aqueous layer was extracted with 10 mL of Et_2O. The total organic layer was washed with 10 mL of saturated NH_4Cl, and dried over Na_2SO_4. The reaction mixture was analyzed by gas chromatography. Toluene and valerophenone (*n*-butyl phenyl ketone) were detected. The peaks had retention times identical to those of authentic samples of toluene and valerophenone.

Tricyclo[4.1.0.0^{1,3}]heptan-4,5-dione (24). To 0.100 g (0.613 mmol) of **22** in 5 mL of CH_2Cl_2 in a Pyrex tube was added 3 mg of Rose Bengal. A 500 W tungsten lamp was placed 15 cm away from the tube, and oxygen was bubbled through the solution. The bottom of the tube was immersed in a dry ice/acetone bath such that most of the tube was exposed to the incident light from the tungsten lamp. The α-enamino ketone **(22)** was consumed in 1.5 h (TLC, 85:15 Et_2O:MeOH), and then the CH_2Cl_2 solution was concentrated to a volume of 0.5 mL. This concentrated solution was passed through a plug of silica gel using Et_2O as the eluant. One product that was UV-active with an R_f = 0.6 (Et_2O) was obtained. Concentration in vacuo gave 3 mg of a yellow solid that was the desired α-diketone (**24**). The compound decomposed upon standing.

24: IR 1751, 1740 cm^{-1}; ^{13}C NMR δ 26.05, 28.33, 30.53, 198.22; CIMS 123 (30), 94 (82), 66 (100).

Benzylidene Acetal of the Diol 27. To 0.170 g (1.35 mmol) of **27** in 3 mL of CH_2Cl_2 was added 0.442 g (2.90 mmol) of benzaldehyde dimethyl acetal. The mixture was stirred for 5 min, and then 15 mg of *p*-toluenesulfonic acid monohydrate was added in one portion. After 6 h, TLC (Et_2O) showed that the diol had been consumed. The reaction mixture was diluted with 7 mL of CH_2Cl_2. The organic solution was washed with 5 mL of 0.1 M NaOH and then dried over Na_2SO_4. After concentration in vacuo, proton NMR analysis of the crude residue showed that two benzylic resonances were present in the spectrum, but the spectrum also showed that benzaldehyde was also present. The benzaldehyde was removed by heating the mixture to 40 °C at 2 Torr for 6 h. Silica gel column chromatography using 4:1 pentane:Et_2O as the eluant gave each epimer of the benzylidene acetal of **27** as clear, colorless liquids.

39a: ^1H NMR δ 1.12−1.15 (m, 1H), 1.23−1.27 (d of d, 1H), 1.52−1.57 (m, 2H), 1.71−1.75 (d of d, 1H), 1.94−1.97 (d of d, 1H), 2.38−2.41 (t of d, 1H), 4.86−4.88 (d, 2H), 5.84 (s, 1H), 7.37−7.53 (m, 5H); GC/MS 214 (15), 185 (43), 167 (37), 141 (28), 129 (84), 115 (64), 91 (81), 84 (67), 79 (100); CIMS 215 (100), 107 (93), R_f = 0.62.

39b: ^1H NMR δ 1.08−1.13 (m, 1H), 1.18−1.21 (d of d, 1H), 1.61−1.64 (t of d), 1.88−1.92 (d of d, 1H), 1.99−2.03 (d of d, 1H), 2.23−2.27 (t of d, 1H), 4.79−4.82 (t of d, 1H), 5.09−5.10 (d of d, 1H), 6.01 (s, 1H), 7.37−7.53 (m, 5H); GC/MS 214 (9), 185 (31), 167 (20), 141 (18), 129 (60), 115 (38), 91 (44), 84 (100), 79 (38); CIMS 215 (100.0), 107 (93.0), R_f = 0.69.

3-[(*N*,*N*-Dimethylamino)methylene]bicyclo[3.1.0]hexan-2-one (32). To 2.0 g (2.1 mmol) of **12** was added dropwise 5.4 g (3.1 mmol) of *tert*-butoxybis(dimethylamino)methane followed by heating in a 70 °C oil bath for 36 h. The viscous, maroon mixture was distilled (0.5 Torr, 35−90 °C) to remove excess Bredereck's reagent. The remaining material was a solid and proved to be 2.8 g (90% yield) of **32**.

32: IR 1688, 1597 cm^{-1}; ^1H NMR δ 0.44−0.48 (q, 1H), 1.02−1.09 (1H, t of d), 1.77−1.81 (2H, d of d), 2.86−2.95 (m, 2H), 2.99 (s, 6H), 7.09 (s, 1H); ^{13}C NMR δ 13.79, 15.39, 26.81, 29.51, 41.90, 99.70, 146.79, 203.4; GC/MS 151 (100), 122 (19), 108 (19), 94 (14); HRMS calcd for $C_9H_{13}NO$ 151.0997, found 151.1000.

3-Diazobicyclo[3.1.0]hexan-2-one (31). To a solution of 0.70 g (4.64 mmol) of **32** in 16 mL of CH_2Cl_2 was added 1.10 g (5.58 mmol) of *p*-toluenesulfonyl azide in one portion. The solution was kept in the dark. After 72 h, the red solution was concentrated by rotary evaporation to give a yellow-orange solid. This solid was washed with 75 mL of a 1:1 pentane:Et_2O solution and then filtered through a funnel containing a glass wool plug to give a yellow filtrate. It was concentrated by rotary evaporation, and silica gel column chromatography using 1:1 pentane:Et_2O as the eluant (R_f = 0.32) gave 0.40 g of **31** as an orange oil.

31: IR 2086, 1681 cm^{-1}; ^1H NMR δ 0.71−0.755 (m, 1H), 1.20−1.27 (m, 1H), 1.78−1.84 (m, 2H), 2.94−3.01 (1H) 3.12−3.26 (1H); GC/MS 122 (100), 94 (12), 66 (82), 39 (85); HRMS calcd for $C_6H_6N_2O$ 122.0480, found 122.0479.

Wolff Rearrangement of the Diazo Ketone 31 in MeOH. A solution of 0.20 g (1.65 mmol) of **31** in 8 mL of MeOH that had been purged with argon was immersed in an ice−water bath that also contained a 450 W medium-pressure mercury arc-lamp. The yellow color of the solution was gone after 3 h of photolysis. Analysis by GC/MS showed that two products with very similar retention times were produced in a 2:1 ratio in 90% yield. These two products were purified by preparative gas chromatography using a column of 13% OV101 on AWDMS at 115 °C. The two products were not separable under these conditions but were determined by ^1H NMR and GC/MS to be a 2:1 mixture of *endo*- and *exo*-2-carbomethoxybicyclo[2.1.0]pentane. The ^1H NMR spectral data were in complete agreement with those reported for these compounds.[9]

Reaction of $LiAlH_4$ with the α-Enamino Ketone 22. To 0.170 g (1.04 mmol) of **22** in 13 mL of Et_2O and 4.0 mL of THF cooled in an ice bath was added 1.2 mL of a 1.0 M Et_2O solution of $LiAlH_4$ over 5 min. The solution was stirred in the ice bath for 30 min. TLC (85:15 Et_2O:MeOH) indicated that the starting material had been consumed and suggested that one product had formed. Excess hydride was then quenched

by careful addition of water. The suspension was diluted with Et_2O to a volume of 50 mL and washed with 20 mL of saturated NH_4Cl and then 20 mL of saturated NaCl. The combined aqueous layer was extracted with 40 mL of Et_2O, and the total organic layer was dried over Na_2SO_4. The Et_2O was removed in vacuo, and silica gel column chromatography of orange residue using 85:15 Et_2O:MeOH as the eluant (R_f = 0.36) gave 0.124 g of 3-hydroxy-4-[(*N*,*N*-dimethylamino)methyl]toluene **(44)** as a clear, colorless liquid that solidified as a white solid when stored at −10 °C.

44: ^{1}H NMR δ 2.30 (s, 3H), 2.33 (s, 6H), 3.61 (s, 2H), 6.59−6.62 (d, 1H, J = 7.5 Hz), 6.67 (s, 1H), 6.84−6.86 (d, 1H, J = 7.5 Hz); ^{13}C NMR δ 21.17, 44.38, 62.53, 116.58, 118.90, 119.61, 128.01, 138.64, 157.79; GC/MS 165 (60), 121 (52), 91 (32), 44 (100); HRMS calcd for $C_{10}H_{15}NO$ 165.1153, found 165.1153.

Attempted Trapping of the Enolate Ion 36. To 0.329 g (2.0 mmol) of 1,1,1,3,3,3-hexamethyldisilazane in 5.1 mL of THF cooled an ice−water bath was added 1.3 mL of a 1.6 M hexane solution of *n*-BuLi dropwise over 5 min. The light tan solution was stirred for an additional 10 min, the flask was cooled to −78 °C, and 0.2 g (1.9 mmol) of **5** in 3.7 mL of THF was added dropwise over 30 min. The solution was stirred at −78 °C for an additional 45 min, and then 0.733 g (2.8 mmol) of *tert*-butyldimethylsilyl trifluoromethanesulfonate in 5.5 mL of THF was added over 2 min. The solution was stirred at −78 °C for 15 min and then added to 20 mL of saturated, aqueous K_2CO_3 and 20 mL of Et_2O. The aqueous layer was extracted with 10 mL of Et_2O. The total organic layer was dried over Na_2SO_4 and then concentrated in vacuo. Analysis by proton NMR and GC/MS showed that the only product obtained from this reaction was the *tert*-butyldimethylsilyl ether of *m*-cresol.

^{1}H NMR: δ 0.20 (s, 6H), 0.99 (s, 9H), 2.31 (s, 3H), 7.09−7.14 (t, 1H), 6.77−6.79 (d, 1H, J = 7.6 Hz), 6.64−6.67 (m, 2H); GC/MS 223 (3), 222 (14), 166 (19), 165 (100).

Reaction of the Enolate Ion 36 with CH_3OD. To 0.329 g (2.0 mmol) of 1,1,1,3,3,3-hexamethyldisilazane in 5.1 mL of THF cooled in an ice−water bath was added 1.3 mL of a 1.6 M hexane solution of *n*-BuLi dropwise over 5 min. The solution was stirred for an additional 10 min and then cooled to −78 °C, and 0.2 g (1.9 mmol) of **5** in 3.7 mL of THF was added dropwise over 30 min. It was stirred at −78 °C for an additional 45 min, and then 2 mL of CH_3OD was added at −78 °C over 1 min. The solution was stirred at −78 °C for 15 min and then added to 20 mL of water and 20 mL of Et_2O. The layers were separated, and TLC (3:1 pentane:Et_2O) showed only one spot with an R_f = 0.55 that was identical to that of the starting material. The organic layer was dried over Na_2SO_4 and then concentrated in vacuo. The ^{1}H NMR spectrum of the crude residue did not display any aromatic or olefinic signals. Silica gel column chromatography using 3:1 pentane:Et_2O as the eluant afforded pure product that by GC/MS, ^{1}H NMR, and ^{2}H NMR was determined to be α-monodeuterated **5-*d*$_a$** and **5-*d*$_b$**.

5-*d*$_a$ and 5-*d*$_b$: IR 1734 cm^{-1}; ^{1}H NMR δ 0.95−1.02 (q, 1H), 1.55−1.61 (d of d, 1H), 1.65−1.75 (t of d, 1H), 1.98−2.02 (t, 1H), 2.16−2.28 (m, 2H), 2.39−2.47 and 2.67−2.70 (1H, ABX), 2.61−2.65 (d of d, 1H); ^{2}H NMR ($CHCl_3$) δ 2.37 (**5-*d*$_b$**), 2.46 (**5-*d*$_a$**); GC/MS 109 (39), 81 (36), 80 (95), 79 (39), 67 (46), 51 (24), 39 (100).

Low-Temperature NMR Observation of 36. In a drybox, 0.341 g (2.04 mmol) of solid LiHMDS was transferred into a 25 mL flask capped with a rubber septum. The flask was removed from the drybox, and then 2.0 mL of THF-d_8 (99.5% atom-d) was added to the flask. A standard NMR tube was capped with a rubber septum and purged with argon, and 280 μL of the 1.0 M THF-d_8 solution of LHMDS was added to the tube by syringe. The tube was placed in the NMR sample tube holder to the required level, and the tube was placed in a dry ice/acetone bath while still under the argon purge. A solution of 0.020 g (0.185 mmol) of **5** in 300 μL of THF-d_8 was added dropwise by syringe to the NMR tube over 2 min. The tube was then quickly taken out of the cold bath and lowered into the probe of the spectrometer that was precooled to −80 °C. The residual THF signal at 3.7 ppm served as the lock frequency, the block size was 32K, and a recycle delay time of 10 s between successive pulses was used to avoid signal/noise problems due to possible saturation broadening. The spectra at −80 °C 5 and 60 min following addition of the ketone were recorded. Then the probe was warmed to −65 °C over 20 min and new signals between 6 and 7 ppm started to appear. The probe was then warmed to −50 °C, and the enolate proton at 4.15 ppm was now gone as were the cyclopropane signals. The peaks at 6−7 ppm were the only peaks in the spectrum. At each temperature where the spectrum was recorded, the fluctuation in temperature was only ±1°.

Matrix Photolysis of the Diazoketones 23 and 31. General Procedure. Samples were prepared by 40:60 dilution of the respective α-diazo ketone with Nujol by weight and layered on a 2.5 cm × 0.3 cm polished NaCl disk. The NaCl disk was then placed in a copper optical sample holder and screwed onto the cooling tip of a Displex closed-cycle helium cryostatic unit. The sample was quickly frozen to 77 K with liquid nitrogen. After the mixture was cooled to 77 K, a vacuum shroud equipped with NaCl optical windows was quickly placed over the sample holder, the sample chamber was evacuated, and the sample was cooled to 15 K. The experiments were carried out at a pressure of 1.0×10^{-5} Torr. The sample was irradiated with a 1000 W xenon arc lamp at a distance of 3 cm from the sample. Due to thermal heating of the sample by the xenon arc, the temperature of the sample was closely monitored during irradiation. When the temperature would reach 20 K, irradiation was briefly interrupted until the temperature of the sample had cooled back down to 15 K. Thus, irradiation was carried out in intervals of 5−15 min at 15−20 K. After each irradiation period, the sample chamber on the Displex was placed into a CW infrared spectrometer. Once irradiation of the sample at 15−20K was completed, the temperature was increased in 20−30 K increments, and the infrared spectra were recorded at these temperatures.

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Supporting Information Available: Calculated energies of reference compounds for group energies and estimation of group equivalents. Analysis of NMR data for compound **28**. NMR data for compounds **5**, **10**, **11**, **18**−**20**, **22**−**24**, **26**, **28**, **31**, **32**, **39**, and **44** (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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