agreement in appearance potentials for loss of H from $C_6H_6$ and $C_6H_4D_2$ (Table I) also indicates the positional integrity of various hydrogen atoms is lost in the fragmenting molecular ion.

It is difficult to understand why a simple bond cleavage reaction is subject to such dramatic fragmentation changes as are observed. One tentative explanation is that the most energetically favorable loss of H is preceded by a slow isomerization reaction, but since little change is observed for other fragmentations of 1,5-hexadiyne, isolated states would be involved. More studies are planned to clarify these points and to test related compounds for similar effects. The ion–molecule chemistry of isomeric $C_6H_6$ cations will be discussed in a full paper.

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## Conformations and Energy Barriers in Medium- and Large-Ring Ketones. Evidence from $^{13}C$ and $^{1}H$ Nuclear Magnetic Resonance

*Sir:*

We wish to report that the $^1H$ and $^{13}C$ nmr spectra[1] of the $C_9$ to $C_{16}$ cycloalkanones, like the spectra of the corresponding cycloalkanes,[2] are strongly temperature dependent in the range of −80 to −170°.

The cmr spectra of the $C_9$–$C_{12}$ cycloalkanones undergo simple changes at low temperatures, as exemplified in Figure 1, which shows the cmr spectrum of cyclodecanone at various temperatures. The resonances of the carbonyl, $\alpha$, and $\epsilon$ carbons in the room-temperature cmr spectrum of the $C_{10}$ ketone have been assigned previously.[3] The carbonyl and $\epsilon$ carbon lines remain unchanged at low temperatures, in agreement with the presence of a single kind of conformation.[4] On the other hand, the $\alpha$, $\beta$, and $\gamma$ carbon resonances are 1:1 doublets at −160°, showing that the single conformation lacks a $C_2$ axis or a plane of symmetry perpendicular to the $C_\alpha$—C=O plane. Thus, the BCB-1 conformation[5] (*i.e.*, boat–chair–boat[6] with the oxygen at C1) cannot be the preferred conformation of cyclodecanone. The BCB-2 and BCB-3 forms (and their mirror images) are both consistent with the nmr data, but the BCB-3 form, which has four transannular H–H repulsive interactions and has the carbonyl group at a "noncorner" position, should be highly favored over the BCB-2 form, which has six such interactions and has the carbonyl group at a "corner" position.[7] Strain energy calculations[8] indeed indicate that the BCB-3 form is of lowest energy.

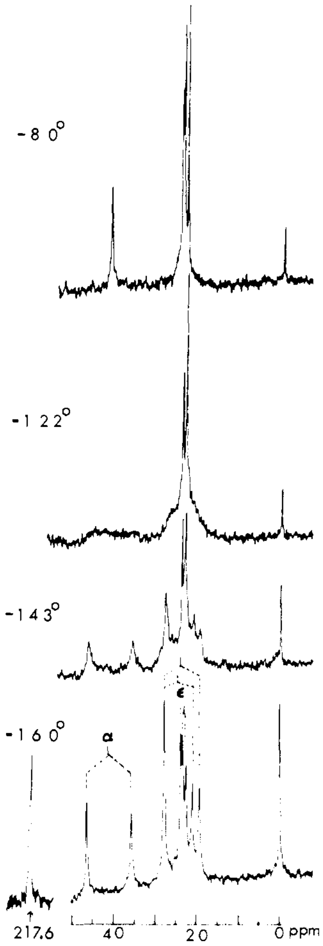
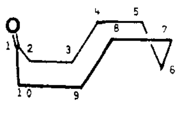
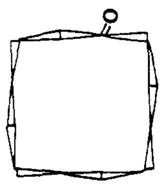


Figure 1. Carbon-13 nmr spectrum (63.1 MHz) of cyclodecanone as a 3% solution in 6:1 $CHCl_2F$–vinyl chloride at various temperatures. The carbonyl band is shown only for the spectrum at −160°. Protons are noise decoupled, and the reference is tetramethylsilane.



BCB-1

BCB-3



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The cmr spectra of the $C_9$, $C_{11}$, and $C_{12}$ cyclic ketones show changes at low temperatures similar to those described for cyclodecanone. Thus, each of these compounds very likely exists in a single kind of conformation, having the same symmetry as mentioned above for

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[1] The nmr spectra (63.1 MHz for $^{13}C$ and 251 MHz for $^1H$) were obtained at a magnetic field of 59 kG. All cmr spectra were obtained by the Fourier-transform technique with protons noise decoupled.

[2] (a) F. A. L. Anet and J. J. Wagner, *J. Amer. Chem. Soc.*, **93**, 5266 (1971). (b) F. A. L. Anet, A. K. Cheng, and J. J. Wagner, *ibid.*, **94**, 9250 (1972); (c) F. A. L. Anet and A. K. Cheng, unpublished work.

[3] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 1347 (1970).

[4] A chiral conformation and its mirror image are taken to be of the same kind in the present discussion.

[5] The chemical shifts at room temperature in the cmr spectrum of cyclodecanone have been considered to support the BCB-1 conformation.[3]

[6] The boat–chair–boat is the preferred conformation of cyclodecane: J. D. Dunitz, *Pure Appl. Chem.*, **25**, 495 (1971).

[7] A corner position is one where the two adjacent dihedral angles have the same signs and about the same magnitudes. A methylene group at a corner position is unhindered and there is thus no relief in nonbonded interactions when that group is replaced by a carbonyl group. Furthermore, the carbonyl oxygen at a corner site is always eclipsed with two hydrogens on the $\alpha$ and $\alpha'$ carbons; this geometry is known[8] to be higher in energy than one where the oxygen is eclipsed with a methylene group, as occurs in the BCB-3 form. In the BCB form the corner sites are 2, 5, 7, and 10.

[8] N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972).

**Table I.** Conformational Energy Barriers in Cyclic Ketones, $(CH_2)_{n-1}C{=}O$

| | $\Delta G^{\ddagger}$, kcal/mol[a] | |
|---|---|---|
| Ring size ($n$) | Cmr spectrum | Pmr spectrum |
| 6 | | 4.0[b] |
| 8 | | 6.3 and 7.5[c] |
| 9 | 5.0 | 5.0 and 6.5 |
| 10 | 6.6 | 6.5 and 7.3 |
| 11 | 5.7 | 6.0 and 6.9 |
| 12 | 7.3 | *ca.* 7.6 |
| 13 | *ca.* 5.8 | *ca.* 5.6 |
| 14 | *ca.* 5.9 | *ca.* 6.3 and *ca.* 6.7 |
| 15 | *ca.* 5.0 | *ca.* 5.0 |
| 16 | *ca.* 5.5 | *ca.* 5.6 |

[a] Errors in $\Delta G^{\ddagger}$ are estimated to be ±0.2 kcal/mol, except where approximate values are given when the errors may be up to ±0.4 kcal/mol. [b] F. A. L. Anet, G. N. Chmurny, and J. Krane, *J. Amer. Chem. Soc.*, **95**, 4423 (1973). [c] F. A. L. Anet, M. St. Jacques, and P. M. Henrichs, *Intra-Sci. Chem. Rep.*, **4**, 251 (1970).

the $C_{10}$ ketone. In cyclotridecanone, the α-carbon resonance is a narrowly spaced doublet at low temperatures, but the other methylene carbons are so overlapped that it is difficult to be certain that there is only one kind of conformation. The cmr spectra of cyclotetradecanone reveal the presence of at least two different kinds of conformations. At −160°, there are two carbonyl bands (intensity ratio 3:2) separated by 1.3 ppm, and the α-carbon resonance is complex. The $C_{15}$ and $C_{16}$ ketones also show evidence for more than one kind of conformation, since the α-carbon resonances in both compounds are ill-defined at low temperatures.

Although the precise conformations of the $C_9$, $C_{11}$, $C_{13}$, $C_{14}$, $C_{15}$, and $C_{16}$ ketones remain unclear, a definite conformation can be assigned to the $C_{12}$ ketone. There is strong evidence that cyclododecane exists virtually exclusively in the "square" ($D_4$) conformation.[2b,9] It appears very likely that the $C_{12}$ ketone has the same ring skeleton as the parent hydrocarbon; symmetry then requires that the carbonyl group be in the noncorner position (I) as would be expected.[7]

Approximate free energy barriers obtained from the cmr spectra of the $C_9$–$C_{16}$ cyclic ketones are given in Table I.

The 251-MHz pmr spectra of the cycloalkanones discussed above are very complicated at low temperatures, but changes in the α- and β-proton resonances can be interpreted in some cases. In cyclodecanone, the α-protons give rise to four chemical shifts (δ 2.04, 2.15, 2.52, 3.41 ppm) at −160°, as expected from the unsymmetrical BCB-3 conformation. Two distinct averaging processes (Table I) are visible as the four α-proton bands change first to two bands (δ *ca.* 2.3 and 2.4) at *ca.* −125° and then to one band above *ca.* −112°. Similar changes are observed for the β protons in cyclodecanone-$\alpha,\alpha,\alpha',\alpha'$-$d_4$.

The lower energy process in cyclodecanone corresponds to that observed in the cmr spectrum (Table I) and is probably a pseudorotation of the BCB-3 *via* the BCB-6 to the mirror image BCB-9. In this process the carbonyl group remains in a favorable site for relieving nonbonded interactions. In order to average the four α-proton resonances of cyclodecanone into one resonance, additional pseudorotation cycles are needed, *e.g.*, BCB-3 → BCB-10 → BCB-7 → BCB-4, and this requires a higher energy, particularly for the BCB-10 to BCB-7 step, as the carbonyl group is forced to remain in the unfavorable corner position during this process.

Cyclododecanone has four α-proton resonances at low temperatures but, in contrast to the $C_{10}$ ketone, these bands coalesce at higher temperatures to a single resonance without passing through a distinct two-resonance region. Two different processes can be envisaged here as in cyclodecanone, but the free energies of activation must be closely comparable. This is reasonable, as nonbonded interactions in the $C_{12}$ ketone should be very much weaker than in the $C_{10}$ ketone.

Two distinct processes can be observed in the pmr spectra of cyclononanone and cycloundecanone (Table I), but in the $C_{13}$, $C_{14}$, $C_{15}$, and $C_{16}$ ketones the spectral changes are too complex for unambiguous interpretation. Nevertheless, approximate $\Delta G^{\ddagger}$'s (Table I) can be obtained. Any process observed in the carbon spectrum must be visible (in the absence of many coincidences) in the proton spectrum, and the data in Table I are in agreement with this requirement.

Highly deuterated as well as $^{13}C$ enriched derivatives of the $C_9$–$C_{16}$ ketones are being synthesized in order to obtain simpler low-temperature nmr spectra. As shown in Table I, all the cycloalkanones from $C_6$ to $C_{16}$ have conformational barriers ≥4 kcal/mol, with the exception of cycloheptanone, which is expected to have a barrier too low for nmr measurement.[8,10]

**Acknowledgments.** We thank Dr. J. J. Wagner for preliminary measurements on the $C_9$ and $C_{10}$ ketones, Dr. T. Ledaal, University of Oslo, and Drs. A. F. Thomas and K. H. Schulte-Elte of Firmenich, Geneva, for gifts of large-ring ketones, and the National Science Foundation for financial support.

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(10) G. Borgen and J. Dale, *Acta Chem. Scand.*, **26**, 3593 (1972).

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## Structure and Thermochemistry of Benzocyclopropenes. The Question of Bond Fixation and Strain Energy

*Sir:*

Although benzocyclopropene (**1**),[1] naphtho[*b*]cyclopropene (**2**),[2] and several of their derivatives[3] have been reported, the important questions of bond fixation and strain associated with these systems remain largely unanswered.[4] We report here the crystal structure of **2** and the thermochemistry of **1** and **2**.

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(1) (a) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965); (b) W. E. Billups, A. J. Blakeney, and W. Y. Chow, *Chem. Commun.*, 1461 (1971).

(2) W. E. Billups and W. Y. Chow, *J. Amer. Chem. Soc.*, **95**, 4099 (1973).

(3) For a comprehensive review see: B. Halton, *Chem. Rev.*, 73, 113 (1973).

(4) An X-ray crystallographic structural analysis of a substituted benzocyclopropene has now appeared. See E. Carstensen-Oeser, B. Muller, and H. Durr, *Angew. Chem.*, **84**, 434 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 422 (1972), and relevant references therein.