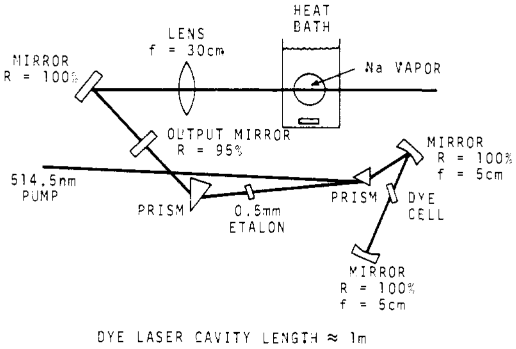

Figure 1. Block diagram of experimental apparatus showing cw dye laser configuration and sodium vapor cell for observing the sodium fluorescence.

dye laser to detect 0.016 fg (1 fg = 10^{-15} g) of sodium vapor.

The apparatus used in these experiments is shown in Figure 1. The laser configuration is similar to that described by Dienes, *et al.*[8] Two prisms and a 0.5-mm uncoated etalon in the cavity reduced the band width of the laser emission to 3 GHz (0.03 Å). The wavelength used in these experiments was 5896 Å and corresponds to the longest wavelength member of the sodium doublet. An output power of approximately 50 mW was obtained when the laser was pumped with 1.7 W of 5140-Å radiation from the Ar ion laser. The laser emission was focused into the sodium cell with a 30-cm focal length lens to give a beam diameter inside the cell of approximately 0.5 mm. The sodium was contained in an evacuated 2-in. spherical flask completely submerged in a well-stirred glycerine temperature bath. The pressure of the sodium vapor was obtained by measuring the temperature of the bath at its coldest point and using the vapor pressure *vs.* temperature data of Gordan.[9] Temperature gradients in the cell were less than 5°. Fluorescence from the sodium vapor in the cell was easily detected by visually observing the narrow line source excited by the passage of the laser beam through the sample cell.

The lowest temperature at which sodium fluorescence was visible was 80°. At this temperature, the vapor pressure of sodium is 1.5×10^{-8} mm.[9] The laser power used in these experiments was sufficient to saturate the sodium transition. This was demonstrated by observing that the intensity of the sodium fluorescence was not appreciably changed when the excitation beam intensity was attenuated by 90%. In this range of excitation intensities, the fluorescence intensity depends only upon the concentration of sodium atoms and not upon the light intensity.

The concentration of sodium atoms at a vapor pressure of 1.5×10^{-8} mm is 4.2×10^{8} atoms/cc. Detection of the fluorescence was actually made in a volume of approximately 1 mm³ which contained 4.2×10^{5} molecules or 0.016 fg of material. Comparison of these data with other fluorescence excitation techniques is shown in Table I. Most of the data for Table I were taken from the recent work of Kuhl and Marowsky.[6] Inspection of Table I shows that the use of a cw organic dye laser as an excitation source for fluorescence analysis decreases the amount of sodium necessary for detection by two orders of magnitude.

Table I. Detectability Limits of Sodium by Different Analytical Techniques[a]

Technique	Limit[b]
Atomic absorption	
Hollow cathode lamp	12 ng/cm³
Pulsed dye laser (sample inside cavity)[c]	2.0 pg/cm³
Atomic fluorescence	
Hollow cathode lamp	33 ng/cm³
Sodium vapor lamp	0.5 ng/cm³
Pulsed dye laser (estimated)[d]	3 pg/cm³
cw dye laser (present work)	16 fg/cm³

[a] See ref 6. [b] Defined by Kuhl and Marowsky[6] as at a concentration where the signal to noise ratio is 2. The limit expressed in the present work is not a true limit in the sense that no signal to noise ratio was determined. [c] See ref 1: 10-cm path with pressure 3×10^{-7} mm ~ 2.0 pg/cm³. [d] Estimated by multiplying 12 ng/cm³ by the ratio of the laser power necessary to obtain a minimum detectable signal in a 12-ng cm³ sample to the maximum laser power available.[6] This assumes that the sodium absorption will not be saturated at the higher laser powers.

Photoelectric detection of fluorescence excited by cw dye lasers will permit quantitative determination of atomic and ionic species in amounts well under a femtogram. Corresponding improvements in the ability to detect molecular species are expected.

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Received August 4, 1972

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(8) A. Dienes, E. P. Ippen, and C. V. Shank, *IEEE J. Quantum Electron.*, 5, 388 (1971).
(9) A. R. Gordan, *J. Chem. Phys.*, 4, 100 (1936).

Determination of Conformational Energy Barriers in Medium- and Large-Ring Cycloalkanes by ^{1}H and ^{13}C Nuclear Magnetic Resonance

Sir:

Until very recently it appeared that only cyclohexane[1] and cyclooctane[2] among the cycloalkanes, $(CH_2)_n$, had conformational energy barriers of magnitudes sufficient for direct measurement by nmr line-shape studies. The successful determination[3] of a conformational barrier in cyclononane by ^{13}C and high-frequency (251 MHz) ^{1}H nmr spectroscopy prompted us to investigate the higher cycloalkanes by these techniques, and we now report measurements of conformational barriers for cyclodecane, cyclododecane, and cyclotetradecane.

The ^{1}H 251-MHz spectra[4] of the C_{10}, C_{12}, and C_{14} cycloalkanes are single lines at room temperature. Below −100°, broadening of the lines occurs and a separation into more than one peak takes place at

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(1) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, 82, 1256 (1960); F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, **41**, 2041 (1964); F. A. L. Anet and A. J. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967).
(2) F. A. L. Anet and J. S. Hartman, *ibid.*, **85**, 1204 (1963); F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, **88**, 2585, 2586 (1966).
(3) F. A. L. Anet and J. J. Wagner, *ibid.*, **93**, 5266 (1971).
(4) The spectra were obtained on a superconducting solenoid nmr spectrometer: F. A. L. Anet, G. W. Buchanan, and C. H. Bradley, paper presented at the 11th Experimental Nuclear Magnetic Resonance Conference, Pittsburgh, Pa., April 1970.

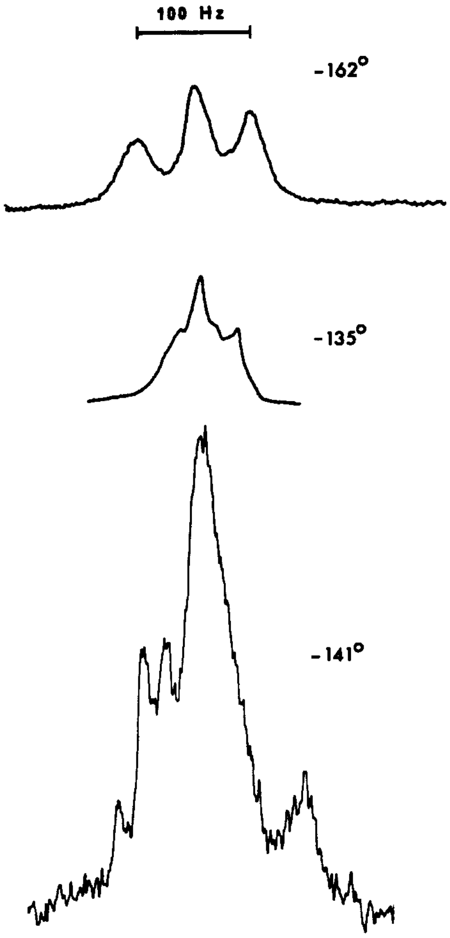


Figure 1. Low-temperature 251-MHz ^1H spectra: top, a 0.4% solution of cyclodecane in CF_2Cl_2; middle, a 0.4% solution of cyclododecane in $CHCl_2F$; bottom, a 0.45% solution of cyclotetradecane in a 3:1 mixture of $CHCl_2F$ and CCl_2F_2, obtained by signal averaging of 16 scans.

−144° for cyclodecane, and at about −120° for the C_{12} and C_{14} hydrocarbons.

The limiting low-temperature proton spectra are shown in Figure 1. Because of their complexities, these spectra are not amenable to analysis for the determination of chemical shifts and coupling constants, nor can accurate rate constants be obtained at intermediate temperatures. Nevertheless, the conformational free-energy barriers must be approximately 6 kcal/mol for cyclodecane and 7 kcal/mol for the other two cycloalkanes. The first number is close to the recently reported barrier of 5.7 kcal/mol in 1,1-difluorocyclodecane.[5]

The 63.1-MHz Fourier-transform ^{13}C spectra[6] of the above three compounds were measured with the protons noise decoupled. The cmr spectra from room temperature down to about −100° were single lines. Limiting spectra for the C_{12} and C_{14} compounds are shown in Figure 2; a limiting spectrum for cyclodecane has not yet been obtained because of the low solubility of this compound at the required temperature (*ca.* −160°).

The cmr spectrum of cyclododecane at −131° consists of two resonances with a chemical-shift separation of 4.8 ppm and an intensity ratio of 2:1. Coalescence of these bands takes place at about −108°. The nmr results are consistent with the "square" conformation (I) of D_4 symmetry determined by X-ray crystallography.[7] Strain energy calculations show that I is the lowest energy conformation for cyclododecane.[8] There are two kinds of carbons, corner (A) and noncorner (B), in I in the ratio of 1:2 in agreement with the cmr results.

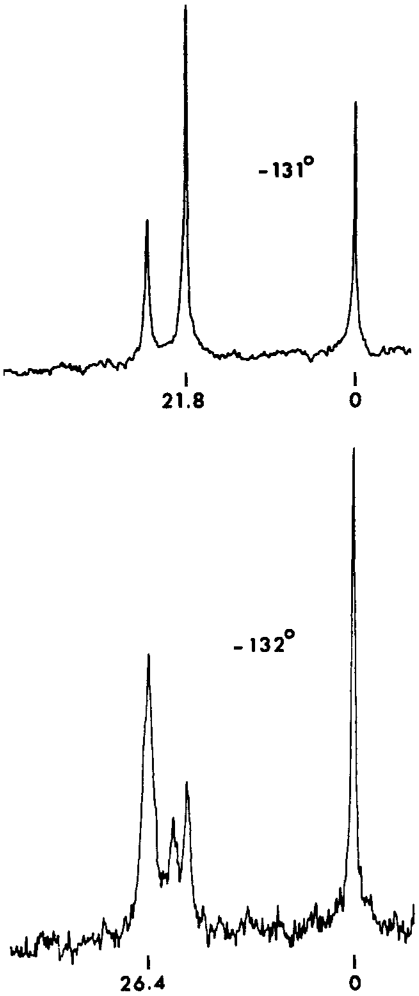
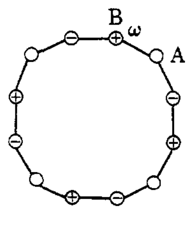
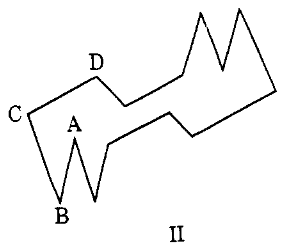


Figure 2. Low-temperature proton-decoupled 63.1-MHz ^{13}C Fourier transform spectra. Chemical shifts are given in parts per million downfield with reference to the tetramethylsilane peak shown at the right of the spectra: top, a 1.2% solution of cyclododecane in a 4:1 mixture of $CH_2{=}CHCl$ and CS_2, 1200 transients; bottom, a 1.2% solution of cyclotetradecane in a 3:2 mixture of CS_2 and $CH_2{=}CHCl$, 2000 transients.

It is likely that the lowest energy mode for conforma-



I



II

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[5] E. A. Noe and J. D. Roberts, *J. Amer. Chem. Soc.*, 94, 2020 (1972).

[6] F. A. L. Anet, V. J. Basus, C. H. Bradley, and A. Cheng, paper presented at the 12th Experimental Nuclear Magnetic Resonance Conference, Gainesville, Fla., Feb 1971.

[7] J. D. Dunitz and H. M. M. Shearer, *Helv. Chim. Acta*, 43, 18 (1960).

[8] K. B. Wiberg, *J. Amer. Chem. Soc.*, 87, 1070 (1965); M. Bixon and S. Lifson, *Tetrahedron*, 23, 769 (1967).

tional transformation in a large ring is asymmetric.[9,10] Models show that a corner and adjacent noncorner carbon atom (*e.g.*, A and B in I) can be moved so that the dihedral angle ω changes sign, with other dihedral angles undergoing the minimum possible change. Similar or identical steps can be carried out successively at the remaining three corner positions.[11] The end result is a mirror-image conformation of I, and the cmr results are consistent with such a process and show that the free-energy barrier is 7.3 kcal/mol.

Cyclotetradecane is thought to be conformationally homogeneous and to have the "rectangular" diamond lattice conformation II,[12] which has four different carbons in the ratio 2:2:2:1. The cmr spectrum at −132° shows lines of approximately 4:1:2 intensity ratio, in agreement with II, provided that two of the different carbons in II have such a small chemical-shift difference that they are not resolved. Pseudorotation[10] of II can proceed by a process analogous to that given for cyclododecane, with opposite corner (C) positions being involved in two successive steps.[13]

Pseudorotation of the type described here for the C_{10}, C_{12}, or C_{14} hydrocarbon results in all the carbons exhibiting a single chemical shift, and the same effect also holds for the protons. Thus, only a single conformational process can be detected in each compound by nmr.

Spectra of the odd-numbered cycloalkanes (n = 11, 13, and 15) remained sharp down to at least −135°. Some broadening occurred a lower temperatures, but separation into more than one peak was not observed. Further work on these compounds is in progress.

Acknowledgments. This work was supported by the National Science Foundation and the U. S. Public Health Service.

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[9] H. B. Hendrickson, *J. Amer. Chem. Soc.*, 89, 7047 (1967).

[10] Semiquantitative calculations by J. Dale, University of Oslo, show that relatively large conformational barriers should be present in the C_{12} and C_{14} cycloalkanes and a much smaller barrier in cyclodecane. (We are most grateful to Professor Dale for sending us copies of manuscripts on this and related topics.)

[11] The overall process is similar to pseudorotation in the cyclooctane boat-chair[2,9] or in the cyclodecane boat-chair-boat (J. D. Dunitz, *Pure Appl. Chem.*, 25, 495 (1971)).

[12] G. Borgen and J. Dale, *Chem. Commun.*, 1340 (1970).

[13] Line-shape studies in this system are in progress. The present results show that $\Delta G^{\ne}$ for cyclotetradecane from the cmr spectra is about 7 kcal/mol at −115°.

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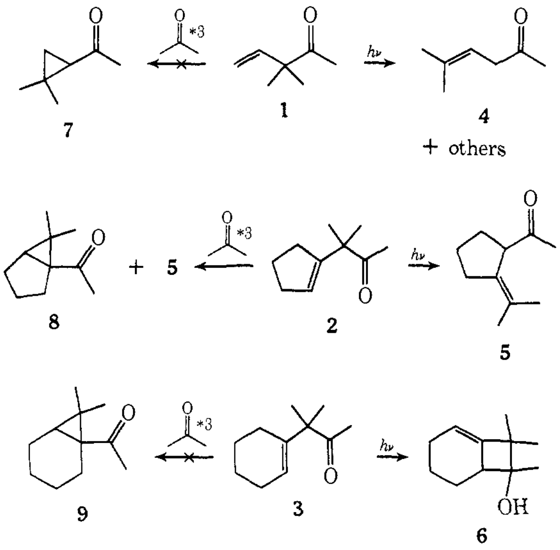
Effect of Ring Size on the Photochemical Behavior of β,γ-Unsaturated Ketones

Sir:

Although β,γ-unsaturated ketones are capable of a variety of photochemical reactions, it is not yet clear what structural features determine the pathway which they will follow.[1] The results reported here demonstrate the delicate balance between acyl shift and γ-hydrogen abstraction in the singlet and show that the triplet behavior of these compounds is strongly affected by the degree to which the double bond is sterically constrained.

We have prepared the closely related compounds **1–3** by reaction of methyllithium with the appropriate carboxylic acid.[2] Scheme I shows the results of irradiating them in benzene at 313 nm and in acetone as triplet sensitizer and solvent. The products **4**, **5**, and **6** were isolated by preparative vpc and their structure determined by nmr and ir spectroscopy: **4**, δ 1.70 (br d, 6 H), 2.01 (s, 3 H), 2.99 (br d, 2 H), 5.24 (br m, 1 H); ir 1719 cm^{-1} (C=O); **5**, 1.65 (br d, isopropylidene), 2.00 (s, methyl ketone), 1.7–2.4 (m, ring protons), 3.37 (br s, methine); ir 1710 cm^{-1} (C=O); **6**, 0.97 (s), 1.16 (s), 1.19 (s) (methyls), 1.3–2.2 (m, ring protons), 5.27 (m, olefin); ir (CCl$_4$) 3600 cm^{-1} (free OH), 1380 (d, *gem*-dimethyl). Compound **7** was prepared from dimethyloxosulfonium methylide and mesityl oxide;[3] no trace of this material could be detected by gas chromatography at 125° of irradiated acetone solutions of **1**. Compound **8** was synthesized independently by photolysis of the pyrazoline[4] from 2-diazopropane and acetylcyclopentene. Its spectral properties were: nmr (CCl$_4$) δ 1.00 (s), 1.08 (s) (methyls), 1.5–2.1 (m, ring protons); ir 1692 cm^{-1} (C=O).

Scheme I



Looking first at the singlet-state photochemistry of **1–3**, one notes that while **1** and **2** undergo an apparent 1,3-acyl shift, **3** proceeds *via* γ-hydrogen abstraction to cyclobutanol **6**. Inspection of molecular models suggests a reason for the difference between **2** and **3**: the much greater distance between the γ hydrogen and the carbonyl oxygen in **2** precludes γ-hydrogen abstraction,[5] leaving acyl shift as a last resort. Although formation of cyclobutanols from β,γ-unsaturated ketones has good precedent,[6] acyl cleavage is a com-

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[1] See R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, 93, 3957 (1971), and references cited therein.

[2] D. B. Bigley and R. W. May, *J. Chem. Soc. B*, 557 (1967).

[3] R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, 89, 1404 (1967).

[4] C. Berger, M. Franck-Neumann, and G. Ourisson, *Tetrahedron Lett.*, 3451 (1968).

[5] N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Shore, *Accounts Chem. Res.*, 5, 92 (1972).

[6] (a) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3671 (1966); (b) E. F. Kiefer and D. A. Carlson, *ibid.*, 1617 (1967); (c) R. C. Cookson, J. Hudec, G. E. Usher, and A. Szabo, *Tetrahedron*, 24, 4353 (1968); (d) R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem Commun.*, 809 (1972); (e) J. C. Dalton, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972, ORGN 97.