## Experimental Section

**General.** All nuclear magnetic resonance spectra were recorded on a Varian Associates A60-A high-resolution nuclear magnetic resonance spectrometer equipped with a variable temperature probe. All chemical shifts are reported as $\delta$ in parts per million downfield from tetramethylsilane. Temperatures were determined from the chemical shift differences between the resonances of ethylene glycol. Integrated intensities were determined electronically on the spectrometer and all values are the average of at least three determinations. Infrared spectra were recorded on a Perkin-Elmer Model 237 recording spectrophotometer. All glpc analyses and separations were carried out on a Varian Aerograph Model 90-P3 chromatograph utilizing a 10 ft × 0.25 in. 15% SE-30 column (60–80 Chromosorb P). The dimethyl sulfoxide-$d_6$ used as the solvent for the equilibrium constant determinations was obtained from Stohler Isotopic Chemicals, Inc. The least-squares calculations on the data presented in Figures 1, 2, and 3 were carried out on a Digital Equipment Corporation Model PDP-8/1 computer.

**2-(*N*-Cyclohexylimino)-1,3-diphenylpropane (1).** A solution containing 21.0 g (0.10 mol) of 1,3-diphenylpropan-2-one and 10.0 g (0.101 mol) of freshly distilled cyclohexylamine in 80 ml of dry benzene was refluxed through a Dean–Stark moisture trap for 24 hr. At this time the theoretical quantity of water (1.8 ml) had been collected in the trap, and the separation of water had apparently ceased. The volatile material was removed by distillation at atmospheric pressure. The residual oil, bp > 230° (0.9 mm), was estimated by nmr (see text) to contain approximately 8% of 1,3-diphenylpropan-2-one as the only detectable contaminant; ir (neat) 3390, 3080, 3060, 2940, 2860, 1715, and 1655 $cm^{-1}$. Partial purification of this oil by preparative glpc provided a light yellow oil which was estimated by nmr to contain 2–3% of 1,3-diphenylpropan-2-one as the only detectable contaminant. This material was used directly for the equilibrium constant determinations.

**Acknowledgments.** We are pleased to acknowledge the Clarkson College of Technology Division of Research for the partial support of this work and the National Science Foundation (GP-6887) for the purchase of the nmr spectrometer. We are grateful to Professor R. R. Andrews for the computer program used in the least-squares calculations.

# Nuclear Magnetic Resonance Spectroscopy. Ring Inversion in γ,γ-Difluoro-ε-caprolactone and γ,γ-Difluoro-ε-caprolactam[1]

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**Abstract:** Fluorine magnetic resonance spectroscopy has been used to determine the rates of ring inversion of γ,γ-difluoro-ε-caprolactone and γ,γ-difluoro-ε-caprolactam. Free energies of activation of 10.0 and 10.4 kcal/mol at −53° were found for the lactone and lactam, respectively. The nmr spectra for both compounds were best interpreted in terms of the chair conformation.

The barriers to ring inversion in saturated seven-membered rings are frequently too low to be determined by the nmr method. The $^{19}F$ nmr spectrum of 1,1,4,4-tetrafluorocycloheptane at −180° shows[3,4] that pseudorotation is still rapid on the nmr time scale at this temperature. With large substituent groups on the ring, as in 1,1-difluoro-4,4-dimethylcycloheptane[3] and 1,1-difluoro-4,5-*trans*-dibromocycloheptane,[5] the barriers become sufficiently large for determination by nmr spectroscopy, but even with these compounds, the free energies of activation are low (5.3 and 7.4 kcal/mol, respectively).

Pseudorotation in cycloheptene is blocked by the presence of the double bond, and ring inversion is considerably slower than for cycloheptane. The enthalpy and entropy of activation for 5,5-difluorocycloheptene were determined[5] to be 7.4 kcal/mol and −0.2 eu, respectively, and a number of other derivatives have been studied.[6] The results for the difluorocycloheptene were interpreted in terms of the chair conformation. Optical rotatory dispersion data[7] for substituted ε-caprolactones have also been interpreted in terms of a chair conformation. Either the chair (**1**) or the boat (**2**) would have been consistent with the requirement

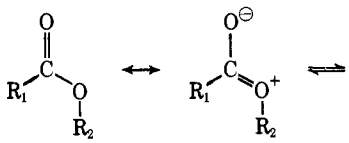
**1** **2**

for a planar lactone function.[8] Pseudorotation of the

(1) Supported by the National Science Foundation.
(2) National Science Foundation Summer Fellow, 1966 and 1968; National Defense Education Act Trainee, 1968–1969.
(3) E. S. Glazer, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1966.
(4) J. D. Roberts, *Chem. Brit.*, 529 (1966).
(5) R. Knorr, C. Ganter, and J. D. Roberts, *Angew. Chem.*, **79**, 577 (1967).
(6) K. von Bredow, H. Friebolin, and S. Kabuss, *Org. Magn. Resonance*, **2**, 43 (1970), and references cited therein.
(7) C. G. Overberger and H. Kaye, *J. Amer. Chem. Soc.*, **89**, 5646 (1967).
(8) Evidence that the lactone function should be planar, or nearly planar, has come from dipole moment studies[9-11] and X-ray structural determinations,[12-19] and for methyl formate by microwave spectroscopy.[20]
(9) R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).
(10) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).
(11) A. Eucken and L. Meyer, *Physik. Z.*, **30**, 397 (1929).
(12) G. A. Jeffrey and S. A. Kim, *Chem. Commun.*, 211 (1966).
(13) A. T. McPhail and G. A. Sim, *J. Chem. Soc. B*, 318 (1966).
(14) J. D. M. Asher and G. A. Sim, *ibid.*, 1584 (1965).
(15) J. F. McConnell, A. McL. Mathieson, and B. P. Schoenborn, *Acta Crystallogr.*, 472 (1964).
(16) B. P. Schoenborn and J. F. McConnell, *ibid.*, **15**, 779 (1962).
(17) J. Fridrichsons and A. McL. Mathieson, *ibid.*, **15**, 119 (1962).
(18) J. F. McConnell, A. McL. Mathieson, and B. P. Schoenborn, *Tetrahedron Lett.*, 445 (1962).
(19) A. McL. Mathieson and J. C. Taylor, *ibid.*, 590 (1961).
(20) R. F. Curl, Jr., *J. Chem. Phys.*, **30**, 1529 (1959).

chair form of ϵ-caprolactone is expected to be slow, relative to the rate for cycloheptane, because the stabilization energy of the ester group is expected to be largely lost by twisting the oxygen to carbonyl carbon bond during the process. Ring inversion in the lactone can also occur as in cycloheptene, without loss of the ester stabilization. The experimental barrier to inversion should then represent a lower limit for each of the possible pathways.

Because pseudorotation of ϵ-caprolactone requires rotation about the oxygen–carbonyl carbon bond, the barrier to ring inversion for this compound could be expected to provide some information about the barrier to cis–trans isomerization in esters. The low concentration of the cis form of most esters has precluded the study of this process by nmr spectroscopy. Huisgen and Ott[9] found that the free energy of activation for the alkaline hydrolysis of ϵ-caprolactone is 3.8 kcal/mol lower than the corresponding value for the 14-membered lactone, and this difference was suggested to be an approximate measure of the cis–trans energy difference in open-chain esters. The equilibrium concentration of the cis conformation at room temperature was calculated to be 0.15%. Estimates of the barrier to rotation about the C–O bond of esters have come from infra-



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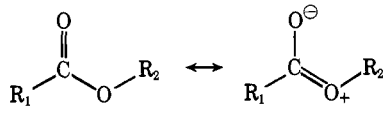

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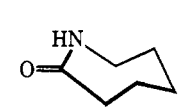
red[21,22] and acoustical[23–28] studies. Pitzer and Miyazawa[21] concluded from an infrared investigation of monomeric formic acid in the vapor phase that the potential maximum for this compound was at 98° from the favored (trans)[29] conformation and was 10.9 kcal/mol above the trans minimum. "Twofold potential barriers" of 13.1 and 15.9 kcal/mol were later obtained by Miyazawa[22] from an infrared study of methyl formate and methyl acetate, respectively. The acoustical method gives values which are quite a bit lower. The activation energy for conversion of the trans form of ethyl formate to the cis form is 5.9 kcal/mol according to Tabuchi,[28] who carried out the first of the quantitative studies. Later estimates are also low. For example, $\Delta H^{\pm}$ and $\Delta S^{\pm}$ for the cis → trans conversion of methyl formate were reported[23] to be 7.8 kcal/mol and −1.8 eu. The corresponding values for ethyl propionate were 1.2 kcal/mol and −18.5 eu.

The most likely conformations of ϵ-caprolactam are the chair and boat forms **5** and **6**, which have essentially planar lactam groups. Formamide has been shown[30] to be almost, but not quite, planar, with a barrier to in-



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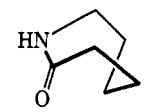

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version at nitrogen of only 1 kcal/mol. Any small deviation from planarity for ϵ-caprolactam will not be important for the present discussion. The results of an esr study[31] of a radical derived from crystalline ϵ-caprolactam have been interpreted as favoring the boat conformation.

We have used the fluorine resonances of γ,γ-difluoro-ϵ-caprolactone (**7**) and γ,γ-difluoro-ϵ-caprolactam (**8**) to obtain information about the rates of inversion in the seven-membered lactone and lactam. The "fluorine-labeling" technique has been found[32] useful for conformational studies of a number of cyclic compounds, and the validity of the method now seems to be reasonably well established.[32k] The two *gem*-fluorides were prepared from 4,4-difluorocyclohexanone.[33] γ,γ-Difluoro-ϵ-caprolactam was obtained by the Schmidt reaction,[34] and oxidation of the ketone with trifluoroperacetic acid[35] afforded the corresponding lactone.

## Experimental Results

The 56.4-MHz $^{19}F$ nmr spectrum of an acetone solution of γ,γ-difluoro-ϵ-caprolactone at ambient temperature is a quintet ($^3J_{HF}$ = 14.5 Hz) centered 1734 Hz upfield from internal ethyl chlorodifluoroacetate. On cooling, the spectrum broadens and splits into an AB pattern. At −85°, the chemical shifts are 1267 and 2018 Hz, and $J_{FF}$ is 240 Hz. Rates of ring inversion at different temperatures were determined by comparison of the experimental spectra with line shapes calculated as a function of $\tau$, the preexchange lifetime. Representative spectra and an Arrhenius plot of ln $1/\tau$ *vs.* $10^3/T$ are shown in Figures 1 and 2. The activation parameters were $\Delta G^{\pm}$ and $\Delta S^{\pm}$ = 10.0 kcal/mol and +8.6 eu at −53°, $E_a$ = 12.4 ± 0.3 kcal/mol, and log $A$ = 15.0 ± 0.3.

The $^{19}F$ nmr spectrum of γ,γ-difluoro-ϵ-caprolactam in acetone at +64° is a quintet ($^3J_{HF}$ = 14.1 Hz) cen-

(21) T. Miyazawa and K. S. Pitzer, *J. Chem. Phys.*, **30**, 1076 (1959).
(22) T. Miyazawa, *Bull. Chem. Soc. Jap.*, **34**, 691 (1961).
(23) J. Bailey and A. M. North, *Trans. Faraday Soc.*, **64**, 1499 (1968).
(24) K. M. Burundukov and V. F. Yakovlev, *Zh. Fiz. Khim.*, **42**, 2149 (1968).
(25) J. E. Piercy and S. V. Subrahmanyam, *J. Chem. Phys.*, **42**, 1475 (1965).
(26) S. V. Subrahmanyam and J. E. Piercy, *J. Acoust. Soc. Amer.*, **37**, 340 (1965).
(27) D. Hall and J. Lamb, *Trans. Faraday Soc.*, **55**, 784 (1959).
(28) D. Tabuchi, *J. Chem. Phys.*, **28**, 1014 (1958).
(29) Some workers, including Pitzer and Miyazawa,[21] have called **4** the cis form when discussing formates. Throughout our discussion, **4** will be taken as the trans form and **3** the cis form for all carboxylic acids and esters, including formates.
(30) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).
(31) M. Kashiwagi and Y. Kurita, *ibid.*, **40**, 1780 (1964).
(32) (a) For discussion and references, see ref 3b; (b) S. L. Spassov, D. L. Griffith, E. S. Glazer, K. Nagarajan, and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 88 (1967); (c) R. Knorr, C. Ganter, and J. D. Roberts, *Angew. Chem.*, **79**, 577 (1967); (d) R. E. Lack, C. Ganter, and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 7001 (1968); (e) R. E. Lack and J. D. Roberts, *ibid.*, **90**, 6997 (1968); (f) R. E. Lack and J. D. Roberts, *ibid.*, **92**, 1107 (1970); (g) G. A. Yousif and J. D. Roberts, *ibid.*, **90**, 6428 (1968); (h) J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *ibid.*, **91**, 1386 (1969); (i) J. E. Anderson and J. D. Roberts, *ibid.*, **92**, 97, (1970); (j) H. J. Reich, E. Ciganek, and J. D. Roberts, *ibid.*, **92**, 5166 (1970); (k) however, see also R. D. Stolow, T. W. Giants, and J. D. Roberts, *Tetrahedron Lett.*, 5777 (1968).
(33) The 4,4-difluorocyclohexanone and 4,4-difluorocyclohexanol used to prepare γ,γ-difluoro-ϵ-caprolactone and γ,γ-difluoro-ϵ-caprolactam were kindly supplied by Dr. G. Berziens of the Explosives Department of E. I. du Pont de Nemours and Co.
(34) R. T. Conley, *J. Org. Chem.*, **23**, 1330 (1958).
(35) W. F. Sager and A. Duckworth, *J. Amer. Chem. Soc.*, **77**, 188 (1955).

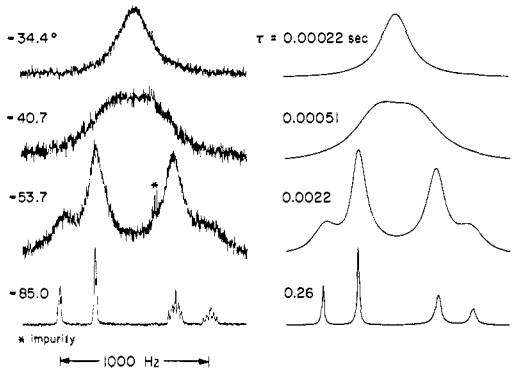



Figure 1. Typical experimental (left) and calculated (right) $^{19}F$ nmr spectra of $\gamma,\gamma$-difluoro-$\epsilon$-caprolactone in acetone; the asterisk denotes impurity.

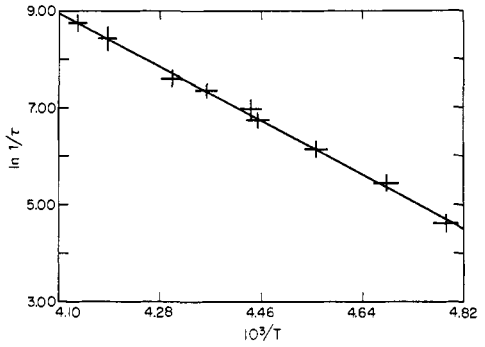



Figure 2. Arrhenius plot for $\gamma,\gamma$-difluoro-$\epsilon$-caprolactone

tered 1653 Hz upfield from ethyl chlorodifluoroacetate, the internal standard. Exchange broadening occurs at the ambient temperature, and on further cooling to −81°, an AB pattern emerges. The chemical shifts are 1026 and 2062 Hz, and $J_{FF}$ is 241 Hz. The compound is much less soluble than the lactone, and the exchange lifetime was obtained at only one temperature (−53°, $\tau$ = 0.0047 sec) where $\Delta G^{\ddagger}$ was calculated to be 10.4 kcal/mol. Spectra taken at −53 and −81° are shown in Figure 3.

The free energies of activation are estimated to be accurate to ±0.2 kcal/mol. Determinations of the values of $E_a$ and $\Delta S^{\ddagger}$ by nmr spectroscopy are known[36] to be subject to systematic errors, and the uncertainty in $E_a$ for the difluoro lactone is probably not well represented by the root-mean-square error. The potentially most serious source of error in the determination of the activation energy for **7** may be the use of the phenomenological $T_2$ (see Experimental Section).

## Discussion

The H–F and F–F coupling constants for both compounds are normal for rings of this size. The axial–equatorial chemical-shift differences of 751 and 1035 Hz found for the lactone and lactam are smaller than the difference of 1602 Hz in 5,5-difluorocycloheptene[5] and are closer to the value[4] for 1,1-difluorocyclohexane (884 Hz). As in 1,1-difluorocyclohexane and most other *gem*-fluorides, the broad, upfield signals in the slow-exchange spectra of Figures 1 and 3 can be assigned to the axial fluorine.

(36) For example, see A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem Soc.*, **88**, 3185 (1966).

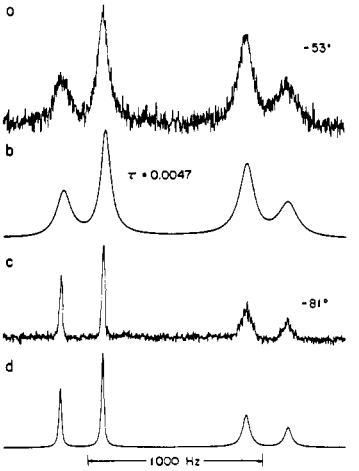



Figure 3. Experimental (a and c) and calculated (b and d) $^{19}F$ nmr spectra of $\gamma,\gamma$-difluoro-$\epsilon$-caprolactam.

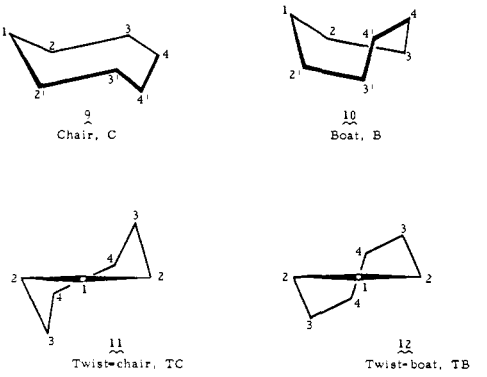


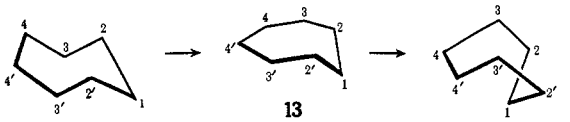

Figure 4. Conformations of cycloheptane.

Because the lactone and lactam studied in this work might undergo ring inversion by processes which occur with either cycloheptane or cycloheptene, it will be desirable to consider some of the possible conformational changes for both. There are two plane-symmetrical forms of cycloheptane, the chair and boat conformations **9** and **10** of Figure 4. The corresponding pseudorotation partners are the twist-chair and twist-boat forms **11** and **12**. Pseudorotation of chair cycloheptane accomplishes complete equilibration of substituent positions in the C and TC forms; according to Hendrickson,[37] the energy profile is a simple sine function, with the twist-chair conformation at the point of minimum energy and the chair conformation at the point of highest energy. The calculated barrier for this process, which also represents the energy difference for the two forms, is only 1.4 kcal/mol. Bixon and Lifson[38] have also calculated a comparable difference (0.67 kcal/mol) for the C and TC conformations.

For cycloheptane, pseudorotation of the chair form will be the process of greatest interest; several other conformational changes will be briefly mentioned here. The TC and TB forms of cycloheptane can be interconverted by an axis-symmetrical process, with a calculated barrier[37] of 8.1 kcal/mol. Boat and chair conformations can be interconverted by two plane-symmetrical processes. Wagging of C-1 to accomplish this inter-

(37) J. B. Hendrickson, *ibid.*, **89**, 7047 (1967).
(38) M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967).

conversion has been described by Hendrickson[37] but the barrier was not calculated. The other plane-symmetrical process involves moving the two 3-carbons upward and the two 4-carbons downward, with the ring passing through a conformation having six coplanar atoms.



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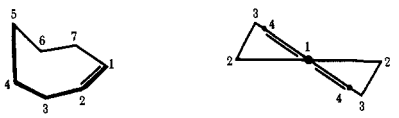
There are also chair and boat conformations of cycloheptene (**14** and **15**). The chair conformation of cyclo-

14 15

tene, unlike chair cycloheptane, is relatively rigid and cannot be converted into other conformations or undergo ring inversion without substantial changes in the bond angles. The boat conformation is more flexible and inversion of this form through conformations **16** and **17** can be accomplished without major deformation



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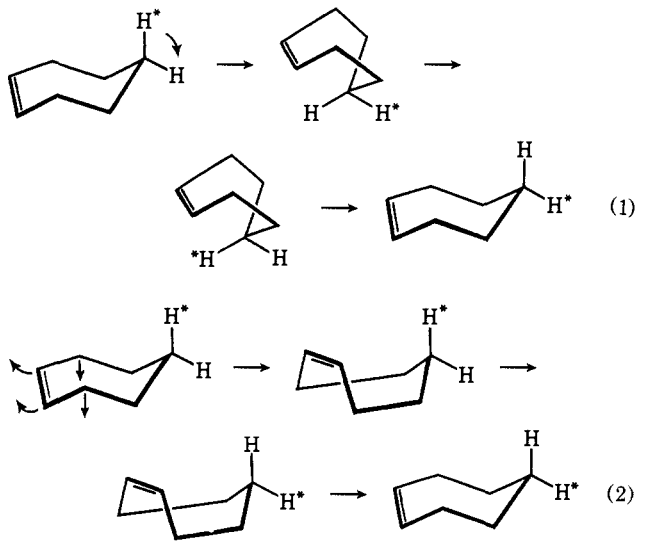
of bond angles. The other two conformational changes of importance are the plane-symmetrical interconversions of the chair and boat forms of cycloheptene. These are analogous to the previously described interconversions of C and B cycloheptane.[39] Chair–chair inversion in cycloheptene can occur by a combination of boat–boat inversion with either of the chair-to-boat processes, as outlined in eq 1 and 2. Molecular models



(1)

(2)

indicate that the equatorial allylic hydrogens in the chair conformation are nearly eclipsed with the alkenic hydrogens, and that this probably unfavorable interaction[40] is partially relieved during C → B conversion by the second route; this effect, along with the large C=C—C bond angles (~125°),[41] suggests that interconversion by eq 2 may be favored in cycloheptene.

The energy required for inversion of boat cycloheptene has been calculated[42] to be 4.4 kcal/mol, but this value is somewhat uncertain because tetrahedral angles were used for the $-CH_2CH_2CH_2-$ units, rather than the more likely values of about 112.5°.[43] Nonetheless, the difference between the calculated barrier and the experimental enthalpy of activation for ring inversion of 5,5-difluorocycloheptene (7.4 kcal/mol)[5] is large enough to suggest that cycloheptene exists in the less flexible chair conformation. Other evidence for a favored chair form of cycloheptene comes from a dipole-moment study of benzocyclohepten-5-one[44,44a] and from nmr studies[6] of benzocycloheptenes and heterocyclic derivatives of cycloheptene.

The barriers for ring inversion of both the difluorolactone and lactam are higher than for 5,5-difluorocycloheptene and are also best interpreted in terms of the chair conformation, in agreement with conclusions based on optical rotatory dispersion measurements,[7] but not the esr spectra for a radical derived from irradiation of crystalline ε-caprolactam.[31,45] The barrier to inversion in the lactam (10.4 kcal/mol) is much smaller than the normal barrier to rotation about the C–N bond of amides (*e.g.*, 18.2 kcal/mol for dimethylacetamide-$d_3$),[46] and this indicates that exchange of equatorial and axial positions does not occur by pseudorotation. As with cycloheptene, it is not known which of the plane-symmetrical C → B interconversion processes occur with the lactams. Nor is the reason apparent for the larger barrier for inversion than for cycloheptene.

The lactone may undergo inversion by the same path as the lactam, but because the energy required to twist the ester group out of planarity is expected to be smaller than for the corresponding process for the lactam, inversion might also occur by pseudorotation. As we have said, the barrier to pseudorotation will be at least as high as the experimental barrier. Several points should be considered in taking the barrier we have observed for the lactone to be a minimum value for cis–trans isomerization of esters in general. (1) The potential barrier for conversion of the stable (trans) form of an open-chain ester to the cis form will be higher than the barrier for the reverse process (more nearly repre-

(39) J. J. Vollmer, Ph.D. Thesis, University of Southern California, Los Angeles, Calif., 1968.

(40) Eclipsing of these hydrogens corresponds to the least stable conformation of propene. The barrier to rotation about the C–C bond in propene is 2 kcal/mol. For references and discussion, see E. Scarzafara and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 310 (1971).

(41) An angle of about 125° is indicated by the magnitude of $^3J$(H–H) for the alkenic protons; see M. A. Cooper and S. L. Manatt, *Org. Magn. Resonance*, **2**, 511 (1970).

(42) G. Favine, G. Buemi, and M. Raimondi, *J. Mol. Struct.*, **2**, 137 (1968).

(43) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7036 (1967).

(44) N. L. Allinger and W. Szkrybals, *J. Org. Chem.*, **27**, 722 (1962).

(44a) NOTE ADDED IN PROOF. The free energy of activation for ring inversion in a deuterated cycloheptene has been recently reported by M. St-Jacques and C. Vaziri, *Can. J. Chem.*, **49**, 1256 (1971), to be 5.0 ± 0.3 kcal/mol at −165°. Although assignment of the chair conformation to benzocycloheptene seems secure (*cf.* also G. L. Buchanan and J. M. McCrae, *Tetrahedron*, **23**, 279 (1967), the conformation of cycloheptene is less certain and, in one study, the boat conformation has been calculated to be more stable by 0.94 kcal/mol (N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **90**, 5773 (1968).

(45) The chair conformation for a substituted ε-caprolactam has been reported as the result of an X-ray diffraction study; V. D. Mootz and B. Berking, *Acta Crystallogr., Sect. B*, **26**, 1362 (1970).

(46) R. C. Neuman, Jr., and V. Jonas, *J. Amer. Chem. Soc.*, **90**, 1970 (1968).

sented by the lactone) by an amount equal to the ground-state energy difference, which appears[9] to be on the order of 3.8 kcal/mol. (2) Even in the absence of the ester stabilization, the chair form and twist-chair forms of the lactone would not have identical energies. However, the eclipsed ethane segment of chair cycloheptane is missing in the lactone, and the nonbonded interactions of the 3a hydrogens in chair cycloheptane may be smaller in the lactone. It seems unlikely that the barrier to pseudorotation in ε-caprolactone would be greatly lowered by this factor. (3) If pseudorotation did not require a very large rotation about the C–O bond, the loss of ester stabilization energy would be less than maximum. Molecular models indicate, however, that the relevant dihedral angle changes by over 90° during the process (105° has been suggested[10] for one of the chair forms of ε-caprolactone). The largest of the calculated[37] dihedral angles for C or TC cycloheptane is 88.1° for one of the TC angles. The point of maximum energy in conversion of a *cis*-ester to the trans isomer probably comes at a dihedral angle somewhat less than 90°, so this factor is unlikely to substantially lower the pseudorotation barrier in ε-caprolactone. We conclude that the values of $\Delta G^{\ddagger}$ and $E_a$ for the lactone are probably best regarded as approximate lower limits for the barriers to conversion of the cis isomer of an open-chain ester to the trans isomer.

If the cis–trans energy difference (2 kcal/mol)[21] is subtracted from the potential barrier (10.9 kcal/mol) for conversion of monomeric *trans*-formic acid to the cis isomer in the vapor phase, and 10% is added as a rough correction[47] for the liquid phase, then the resulting value (10 kcal/mol) is quite similar to the barriers in the lactone. Corresponding corrections for the barriers obtained[22] by the infrared method for methyl formate and methyl acetate (13.1 and 15.9 kcal/mol) would bring these values also into fair agreement with the barrier for the lactone.

## Experimental Section

Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken on a Büchi melting point apparatus and are uncorrected.

Infrared spectra were taken on a Beckman IR-7 spectrometer. Proton and fluorine nmr spectra were obtained with the Varian A-56/60A spectrometer. Proton chemical shifts are reported in parts per million downfield from internal tetramethylsilane. The fluorine nmr spectra were calibrated by the side-band technique using a Lenkert Model 6200 DS audiooscillator and a Hewlett-Packard Model 5216A counter. The signal-to-noise ratio of the low-temperature fluorine spectra was improved with a time-averaging computer, Varian Model C-1024; up to 11 scans were required. The Varian Model V-6040 variable-temperature accessory was used to control the temperature. The methanol chemical-shift difference was used to determine the temperatures for γ,γ-difluoro-ε-caprolactone above −65°. The other temperatures were measured by replacement of the sample tube with an open tube containing a suitable solvent and a copper-constantan thermocouple.

Theoretical spectra were generated by an IBM 360/75 computer using the Gerig program[48] which is based on the equations of Alexander.[49] The parameters used in calculation of the spectra included a chemical shift, a mean lifetime, $\tau$, and an "effective" relaxation time, $T_2$, for each nucleus in the system. The relaxation times were selected to reproduce, as far as possible, the line shapes in the spectra taken at the slow-exchange limit. The values of $\tau$ were determined by comparison of the calculated and experimental spectra.

Ethyl chlorodifluoroacetate was used as an internal standard for the fluorine nmr spectra. The concentrations of the two solutions were: γ,γ-difluoro-ε-caprolactone, 21% by weight in acetone; γ,γ-difluoro-ε-caprolactam, 9% by weight in acetone.

**γ,γ-Difluoro-ε-caprolactone.** The oxidation was carried out by a procedure similar to the one described by Duckworth and Sager[35] for the preparation of ε-caprolactone from cyclohexanone. Hydrogen peroxide (90%) (0.82 g) was added dropwise with stirring at 5–10° to 6.0 g of trifluoroacetic anhydride. 4,4-Difluorocyclohexanone[33] (2.8 g, 21 mmol) was melted and added dropwise with stirring at a temperature of 10–15°. After the addition was complete, the mixture was stirred at 10–15° for 10 min and at 8° for 15 min. Isolation of the product[35] afforded crude material which was purified by sublimation at a pressure of 0.2 mm and a bath temperature of about 70°. The yield after five sublimations was 1.6 g, collected in two fractions. The first fraction of 1.3 g had mp 71.3–72.4°; ir ($CCl_4$) 1757 and 1164 $cm^{-1}$. The pmr spectrum showed multiplets at δ 1.9–3.0 (6 H) and 4.25–4.5 (2 H). The mass spectrum showed the parent ion at *m/e* 150.

*Anal.* Calcd for $C_6H_8F_2O_2$: C, 48.00; H, 5.37; F, 25.31. Found: C, 47.96; H, 5.32; F, 25.41

**4,4-Difluorocyclohexanone.** A solution of 2.0 g of 4,4-difluorocyclohexanol[33] in 45 ml of acetone was cooled to 5° in an ice bath, and Jones reagent[50] was added dropwise with stirring. The solution was stirred at room temperature for 45 min, poured into ice water, and extracted five times with 90-ml portions of ether. The combined ether portions were washed with saturated sodium bicarbonate solution, and most of the ether was removed by distillation through a Vigreux column at atmospheric pressure. The flask was evacuated briefly at the rotary evaporator, giving a residue of 1.3 g. A vapor-phase chromatogram showed the presence of unreacted alcohol, in addition to the ketone. The ir spectrum ($CCl_4$) showed carbonyl absorption at 1724 $cm^{-1}$ [lit.[32d] ($CHCl_3$) 1724 $cm^{-1}$]. The crude product was used in the next step without further purification.

**γ,γ-Difluoro-ε-caprolactam.** Polyphosphoric acid[51] (25 ml) was placed in a flask containing the 1.3 g of crude ketone, and 0.77 g of sodium azide was added in small portions over a period of 5 min.[34] The temperature was raised to 50° after 20 min and was increased to 70° after 23 hr. Seventy-one hours after the reac ion was started, the mixture was cooled to room temperature and poured with stirring into 175 ml of ice water. Cold 50% sodium hydroxide was added with cooling and stirring until a pH of about 8 was reached, and the lactam was extracted with six 100-ml portions of chloroform. The solution was dried over $MgSO_4$ and the solvent was removed by distillation. The residue, an orange-brown solid, was sublimated five times at 0.2 mm and 70–80° and afforded a total of 0.45 g, collected in three fractions: a first fraction of impure light-yellow solid (94 mg); a second fraction of white solid (114 mg; mp 105–106°); and a third fraction of white solid (241 mg, mp 105.5–106.5°), the latter of which was used for the spectral and elemental analyses. The ir spectrum ($CCl_4$) showed absorption at 725 (weak, broad), 1677 (strong), 3095, 3220, 3305, and 3422 $cm^{-1}$. The pmr spectrum of a hexadeuterioacetone solution showed a broad peak centered at δ 7.35 (N–H), a multiplet centered at 3.25 ($NCH_2$), and a series of peaks between 3.0 and 1.7 arising from the remainder of the hydrogens. The mass spectrum showed the parent ion at *m/e* 149.

*Anal.* Calcd for $C_6H_9F_2NO$: C, 48.32; H, 6.08; F, 25.48. Found: C, 48.26; H, 6.10; F, 25.44.

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