Imine–Enamine Tautomerism. I. 2-(*N*-Cyclohexylimino)-1,3-diphenylpropane

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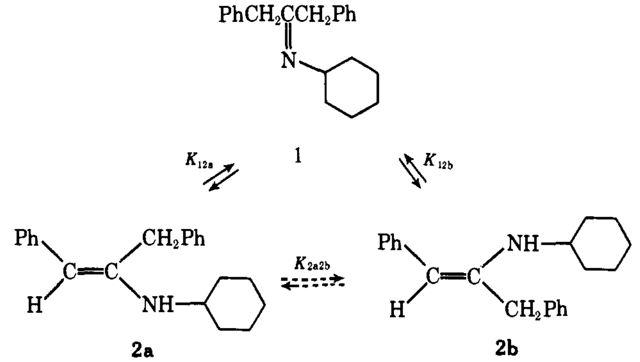
Abstract: A thermodynamic study of the tautomerization of 2-(*N*-cyclohexylimino)-1,3-diphenylpropane to its enamine tautomers *cis*- and *trans*-2-(*N*-cyclohexylamino)-1,3-diphenylpropene in the solvent dimethyl sulfoxide-d_6 is reported. The equilibrium constants and the values of the thermodynamic parameters ΔH, ΔG, and ΔS have been determined by variable temperature nuclear magnetic resonance measurements over the temperature range of 310–411°K. The extrapolated values for these parameters are for the imine-*cis*-enamine tautomerism, $\Delta H_{298} = -1.9$ kcal/mole, $\Delta G = 0.74$ kcal/mole, and $\Delta S = -8.9$ cal/(mole deg); for the imine-*trans*-enamine tautomerism, $\Delta H = -2.6$ kcal/mole, $\Delta G = 0.34$ kcal/mole, and $\Delta S = -10.0$ cal/(mole deg); and for the cis–trans isomerization of the enamine tautomers, $\Delta H = 0.59$ kcal/mole, $\Delta G = 0.39$ kcal/mole, and $\Delta S = 0.69$ cal/(mole deg). Polar solvents favor enaminization; however, there appears to be little effect of solvent on the cis–trans isomerization of the enamine tautomers.

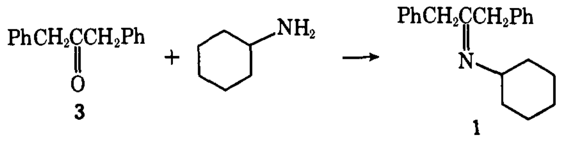
Although the keto–enol tautomerism has been thoroughly investigated for a large number of systems, the related imine–enamine tautomerism has been observed and measured for only a few isolated systems.[2,3] We report here the direct observation of such a tautomerism by nuclear magnetic resonance methods and the determination of the values of the thermodynamic parameters ΔH and ΔG and ΔS from the equilibrium constants determined at various temperatures.

A careful examination of the structure of the systems for which the imine–enamine tautomerism has been observed reveals that a special stabilization, generally conjugative in nature, of the carbon–carbon double bond of the enamine tautomer is apparently required for a tautomer composition in which the enamine attains a concentration sufficiently large to be quantitatively determined by spectroscopic techniques. In certain of the systems for which this tautomerization has been observed, the enamine tautomer may be further stabilized by hydrogen bonding through chelate formation.[3] We therefore anticipated that the enaminization of 2-(*N*-cyclohexylimino)-1,3-diphenylpropane (**1**) might occur to a measurable extent due to the conjugative stabilization of the cis and trans enamine tautomers, **2a** and **2b**, respectively, by the phenyl substituents (Scheme I).[4] Furthermore, the symmetry of this system with respect to the two possible directions of enaminization, *i.e.*, migration of the double bond into the 1,3-diphenylpropane backbone, substantially simplifies the analysis of the data and obviates the necessity of the consideration of the syn–anti imine isomerization.[5]

Scheme I



2-(*N*-Cyclohexylimino)-1,3-diphenylpropane (**1**) is obtained in good yield as a high-boiling viscous liquid contaminated with 5–10% of 1,3-diphenylpropan-2-one (**3**) by the condensation of **3** with cyclohexylamine. The partial purification of the imine (**1**) was effected by preparative gas–liquid phase chromatography (glpc). Minor quantities of the ketonic contaminant (**3**) of approximately 2 or 3% as estimated from the nmr spectrum could not be removed from the imine.[6] The presence of the ketone was also indicated by the observation of weak carbonyl absorption in the infrared spectrum at 1715 cm^{-1}. Although cyclohexylamine was not detected as a contaminant in the imine purified in this way, it is conceivable that the ketone present arises from trace amounts of hydrolysis occurring in the purification procedure.



The 60-MHz nmr spectrum of 2-(*N*-cyclohexylimino)-1,3-diphenylpropane (**1**) as an approximately 1 *M* solution in dimethyl sulfoxide-d_6 at the ambient temperature of the nmr probe exhibited absorptions at δ 7.35, 6.5,

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(1) Author to whom inquiries should be directed.

(2) (a) J. Harley-Mason and T. J. Leeney, *Proc. Chem. Soc., London*, 368 (1964); M. Israel, L. C. Jones, and E. J. Modest, *J. Heterocycl. Chem.*, **4**, 659 (1967); (c) H. Bredereck, G. Simchen, R. Wahl, and F. Effenberger, *Chem. Ber.*, **101**, 512 (1968); (d) H. Albrecht, *Tetrahedron Lett.*, 4421 (1968); (e) H. Albrecht, J. Blecher, and F. Kröhnke, *ibid.*, 439 (1969).

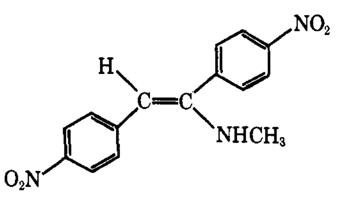
(3) (a) G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 2099 (1961); (b) G. O. Dudek and R. H. Holm, *ibid.*, **83**, 3914 (1961); (c) S. Forsén and M. Nillson, *Ark. Kemi*, **19**, 569 (1962).

(4) The arrows indicating the direct cis–trans isomerization **2a** to **2b** and *vice versa* have been inserted as dotted to indicate that while an equilibrium constant for this process can be defined and measured, this geometrical isomerization almost certainly proceeds *via* the intermediacy of the imine tautomer.

(5) D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, **83**, 3474 (1961).

(6) Due to the sensitivity of 2-(*N*-cyclohexylimino)-1,3-diphenylpropane toward autoxidation, purification is difficult and all operations must be carried out under a dry nitrogen atmosphere.

4.5, 3.9, 3.5, and 0.7–2.2 in ppm downfield from tetramethylsilane as the internal standard. The relatively high concentration of substrate was employed in order to obtain more accurate integrated areas of the individual absorptions. Quantitative nmr measurements on solutions of concentration significantly higher than 1 *M* were of questionable value due to substantial broadening of the absorption lines accompanied by a loss of resolution. A singlet absorption at δ 3.9, the intensity of which varied somewhat depending upon the origin of the sample, was shown to arise from the α-methylene protons of the contaminant, 1,3-diphenylpropan-2-one (**3**), by comparison of the chemical shift of the corresponding protons of authentic **3** in dimethyl sulfoxide-d_6. No evidence for the enolization of this ketone in dimethyl sulfoxide-d_6 was observed within the limits of the sensitivity of the nmr method. This is not unexpected in view of the observation that imines generally enaminize more readily than ketones enolize.[3,7] The absorptions at δ 6.5 and 5.5 were assigned to the vinylic protons of the cis and trans enamine tautomers, **2a** and **2b**, respectively, and the broad absorption centered at approximately δ 4.5 was assigned to the proton bonded to nitrogen in the enamine tautomers. These assignments are based both on the basis of comparisons with the previous assignments in related compounds[2d,2e] and on the observation that the integrated area of the δ 4.5 absorption was consistently equivalent to the sum of the integrated areas of the two absorptions in the vinyl region of the spectrum. The assignment of the δ 6.5 and 5.5 absorptions to the vinyl protons in **2a** and **2b**, respectively, rather than the reverse assignment, is somewhat less certain. Two factors were considered in making these assignments. First, in general olefinic protons oriented in a cis geometry with respect to electronegative atoms substituted on a double bond, *e.g.*, halogen atoms, absorb at lower field than those in the trans arrangement;[8] and second, Albrecht[2e] has observed the chemical shift of the vinyl proton absorption in 1-(*N*-methylamino)-*p*,*p*′-dinitrostilbene (**4**), in which the aryl groups and hence the vinyl proton and the methylamino substituents are almost certainly trans, as δ 5.5. In the absence of further information, we are of the opinion that these are the most reasonable assignments.



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The equilibrium constants for the processes outlined in Scheme I were determined at eight temperatures over the range of 310–411° K by variable temperature nmr measurements. The cis and trans enamine tautomer concentrations could be determined relative to the total substrate concentration from the ratio of the integrated areas of the vinyl proton absorptions at δ 6.5 and 5.5 to that of the cyclohexyl proton absorption at δ 0.7–2.2.

The total enamine concentration (realtive to the concentration of the imine) can be determined either from the sum of the integrated areas of the two absorptions in the olefinic region of the nmr spectrum or from the integrated area of the rather broad NH absorption centered at approximately δ 4.5 but extending over the range of approximately δ 4.2–4.8 at the ambient temperature of the nmr probe. The sum of the equilibrium constants for enaminization K_{12a} and K_{12b} (K_e defined by eq 1) can thus be determined in two different ways from the nmr data. The equilibrium constant for the cis–trans isomerization of the enamine tautomers (K_{2a2b} defined by eq 2) was determined directly from the ratio of the integrated areas of the absorptions in the vinyl region of the nmr spectrum. The values of the equilibrium constants for enaminization (K_{12a} and K_{12b} defined by eq 3 and 4, respectively; see Scheme I) were calculated from eq 5 and 6 obtained from the combination of eq 1–4.

$$K_e = K_{12a} + K_{12b} = \frac{[2a] + [2b]}{[1]} \tag{1}$$

$$K_{2a2b} = \frac{[2a]}{[2b]} \tag{2}$$

$$K_{12a} = \frac{[2a]}{[1]} \tag{3}$$

$$K_{12b} = \frac{[2b]}{[1]} \tag{4}$$

$$K_{12a} = \frac{K_e K_{2a2b}}{K_{2a2b} + 1} \tag{5}$$

$$K_{12b} = \frac{K_e}{K_{2a2b} + 1} \tag{6}$$

Although the two methods of determination of K_e from the nmr data gave comparable results, the values of the equilibrium constants reported here are based on K_e as determined from the sum of the integrated areas of the vinyl proton absorptions as a result both of the inability to obtain accurate integrated areas of the rather broad NH absorption band and due to the observation that the chemical shift of this NH absorption was temperature dependent, overlapping somewhat with the δ 3.9 absorption of the 1,3-diphenylpropan-2-one at the higher temperatures.

In Table I is presented the value of K_e at the various temperatures employed.

Table I. Sum of the Equilibrium Constants for the Enaminization of 2-(*N*-Cyclohexylimino)-1,3-diphenylpropane in Dimethyl Sulfoxide-d_6 as a Function of Temperature

T, °K	$K_e = K_{12a} + K_{12b}$
310	0.73
320	0.58
331	0.59
342	0.51
354	0.46
365	0.44
378	0.34
411	0.30

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(7) H. Hanecka, "Chemie der Beta-Dicarbonylverbindungen," Springer-Verlag, Berlin, 1950, p 189.

(8) For representative spectra see N. S. Bhacca, L. F. Johnson, and J. N. Schoolery, "High Resolution, NMR Spectra Catalog," Vol. 1, Varian Associates, Palo Alto, Calif., 1962, Spectra 17, 18, and 23.

Table II. Equilibrium Constants and Thermodynamic Quantities for the Cis–Trans Isomerization of 2-(*N*-Cyclohexylamino)-1,3-diphenylpropene in Dimethyl Sulfoxide-d_6 as a Function of Temperature

T, °K	K_{2a2b}[a]	ΔG, kcal/mol[b]	ΔS, cal/(mol deg)[b]
298	0.52[c]	0.39	0.69
310	0.53	0.39	0.65
320	0.56	0.37	0.69
331	0.59	0.35	0.73
342	0.59	0.36	0.68
354	0.61	0.35	0.68
365	0.63	0.34	0.70
378	0.66	0.32	0.73
411	0.67	0.33	0.64

[a] The value of ΔH is 0.59 kcal/mol with a standard deviation of 0.06 kcal/mol. [b] The standard deviations in the values of ΔG and ΔS are 0.08 kcal/mol and 0.15 cal/(mol deg), respectively. [c] The value of K_{2a2b} at 298°K was determined by extrapolation of the least-squares line of Figure 1. The accompanying thermodynamic quantities at this temperature are calculated on the basis of this extrapolated value.

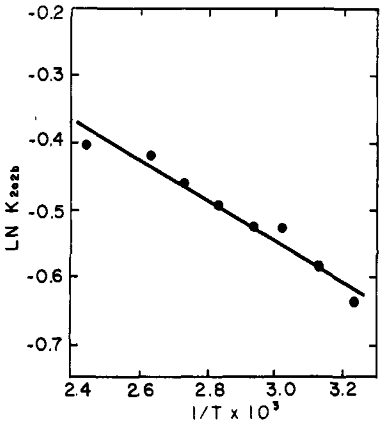

Figure 1. Variation of the natural logarithm of the equilibrium constant for the cis–trans isomerization of 2-(*N*-cyclohexylamino)-1,3-diphenylpropene in dimethyl sulfoxide-d_6 with the reciprocal of the absolute temperature.

Table III. Equilibrium Constants and Thermodynamic Quantities for the *cis*- and *trans*-2-(*N*-Cyclohexylamino)-1,3-diphenylpropene–2-(*N*-Cyclohexylimino)-1,3-diphenylpropane Tautomerizations in Dimethyl Sulfoxide-d_6 as a Function of Temperature

T, °K	K_{12a}[a]	ΔG, kcal/mol[f]	ΔS, cal/(mol deg)[b]	K_{12b}[c]	ΔG, kcal/mol[d]	ΔS, cal/(mol deg)[d]
298	0.29[e]	0.74	−8.9	0.57[e]	0.34	−10.0
310	0.25	0.85	−8.9	0.48	0.45	−10.0
320	0.21	0.99	−9.0	0.37	0.63	−10.0
331	0.22	1.0	−8.8	0.37	0.65	−10.0
342	0.19	1.1	−8.8	0.32	0.77	−10.0
354	0.17	1.2	−8.9	0.29	0.87	−9.9
365	0.17	1.3	−8.7	0.27	0.95	−9.8
378	0.14	1.5	−8.9	0.20	1.2	−10.0
411	0.12	1.7	−8.8	0.18	1.4	−9.9

[a] The associated value of ΔH is −1.9 kcal/mol with a standard deviation of 0.10 kcal/mol. [b] These are the values for the imine–*cis*-enamine tautomerism. The standard deviations of ΔG and ΔS are 0.05 kcal/mole and 0.4 cal/(mol deg), respectively. [c] The associated value of ΔH is −2.6 kcal/mol with a standard deviation of 0.12 kcal/mol. [d] These are the values for the imine–*trans*-enamine tautomerism (K_{12b}). The standard deviations of ΔG and ΔS are 0.05 kcal/mol and 0.60 cal/(mol deg), respectively. [e] The values of K_{12a} and K_{12b} at 298°K were determined by extrapolation of the least-squares lines of Figures 2 and 3, respectively. The accompanying thermodynamic quantities at this temperature are calculated on the basis of this extrapolated value. [f] See ref 6.

In Table II is presented the value of the equilibrium constant for the cis–trans isomerization of the enamine tautomers at various temperatures as determined directly from the nmr data. In addition Table II gives the value of ΔH, as determined from the least-squares slope of the plot of the natural logarithm of the equilibrium constant K_{2a2b} against the reciprocal of the absolute temperature (Figure 1), the values of ΔG as determined from eq 7, and the values of ΔS as deter-

$$\Delta G = -RT \ln K \qquad (7)$$

mined from eq 8. Although the cis–trans isomeriza-

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (8)$$

tion of the enamines (**2a** $\rightleftarrows$ **2b**) is almost certainly not a direct isomerization but requires the intermediacy of the imine (**1**), the observation that the respective imine–enamine tautomeric equilibria are apparently attained (*vide infra*) requires that the values of the associated thermodynamic parameters reported in Table II reflect the respective differences between the cis and trans enamine tautomers *under these conditions.*

A careful examination of Figure 1 reveals some scattering of the points from the least-squares line. This is almost certainly an indication of the relatively low sensitivity of the nmr method. There is, however, no apparent tendency for the development of curvature in this graphical representation, and thus it appears that, at least within the sensitivity of this method of analysis, the value of ΔH is constant over the range of temperatures studied. The absence of curvature would also appear to indicate that equilibrium has been attained. This was further confirmed by repeating the measurements at the lower temperatures over periods of up to 2 hr. The equilibrium constants were found to be invariant over this period of time. Thus it appears that equilibrium is quite rapidly attained and consequently that the rates of enaminization are relatively rapid.

The values of the equilibrium constants for enaminization K_{12a} and K_{12b} calculated from eq 5 and 6, respectively, at the various temperatures are presented in Table III. In addition the corresponding values of ΔH, determined from the least-squares slope of the plots of the natural logarithm of K_{12a} and K_{12b} against the reciprocal of the absolute temperature (Figures 2 and 3, respectively), the values of ΔG calculated from

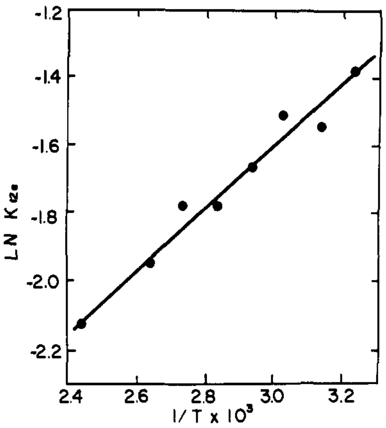

Figure 2. Variation of the natural logarithm of the equilibrium constant for the 2-(*N*-cyclohexylimino)-1,3-diphenylpropane–*cis*-2-(*N*-cyclohexylamino)-1,3-diphenylpropene tautomerism in dimethyl sulfoxide-d_6 with the reciprocal of the absolute temperature.

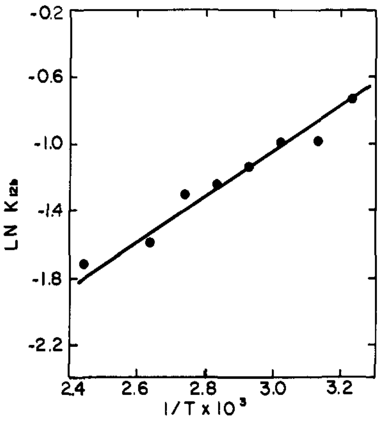

Figure 3. Variation of the natural logarithm of the equilibrium constant for the 2-(*N*-cyclohexylimino)-1,3-diphenylpropane–*trans*-2-(*N*-cyclohexylamino)-1,3-diphenylpropene tautomerism in dimethyl sulfoxide-d_6 with the reciprocal of the absolute temperature.

eq 7, and the values of ΔS calculated from eq 8 are included.

Discussion

The direct observation of the tautomerism of an imine to its cis and trans enamine tautomers and the determination of the equilibrium constants and the corresponding values of the thermodynamic parameters for these equilibrium processes have not to our knowledge been previously reported. It is, however, quite apparent that, at least for the imine–enamine tautomerizations, care should be exercised in the attachment of too much significance to the equilibrium constants and thermodynamic quantities determined in this work. The equilibrium constants K_{12a} and K_{12b} for the imine–*cis*-enamine and imine–*trans*-enamine tautomerizations appear to be rather solvent sensitive. For example, the value of K_e, the sum of the equilibrium constants K_{12a} and K_{12b}, falls from a value of 0.73 in dimethyl sulfoxide-d_6 at 310°K (see Table I) to a value of approximately 0.05 in tetrachloroethylene at the same temperature. This decrease in the equilibrium constants for enaminization with a decrease in the solvating ability of the solvent is not too surprising in view of the expectation that the enamine tautomers would themselves exhibit appreciably greater polar character than the imine and hence be more efficiently stabilized by solvation effects in the more polar solvents. Thus, the rather strongly solvating solvent dimethyl sulfoxide-d_6 would be expected, as is observed, to be effective in shifting the tautomeric equilibria in the direction of the isomeric enamines. It is, therefore, abundantly clear that differential solvation factors play an important role in the determination of the equilibrium constants and thermodynamic quantities associated with the enaminization processes in highly solvating solvents such as dimethyl sulfoxide-d_6, and thus the values of the thermodynamic parameters for the enaminizations reported in this work probably do not reflect the differences inherent in the imine and enamine tautomeric forms.

The question as to the extent to which differential solvation effects may play a role in determining the relative proportions of the cis and trans enamine tautomers is a rather more difficult one to answer on the basis of the presently available evidence. Qualitatively it is to be expected that the isomeric enamines should show a substantially greater similarity in their susceptibility to solvation in a solvent such as dimethyl sulfoxide-d_6 than the imine–enamine tautomers. Consequently it is not unreasonable to expect that if such solvation effects are operative in determining the relative proportions of the cis and trans enamine tautomers at equilibrium, they are of considerably less importance than in the imine–enamine tautomerisms. Although the equilibrium constant K_{2a2b} for the cis–trans isomerization of the enamines is rather difficult to quantitatively evaluate in tetrachloroethylene due to the relatively small amounts of these species present (*vide supra*), it appears that the relative proportion of the cis and trans enamine tautomers is virtually unaffected by this change in solvent. Therefore, it is quite probable that the values of the thermodynamic parameters reported for the cis–trans isomerization of the enamine tautomers **2a** and **2b** (Table II) are a rather accurate representation of the differences inherent in these two geometric isomers. We anticipate that the studies involving systematic solvent variation currently in progress will serve to more precisely define the role of the solvent in determining the equilibrium positions of these processes.

The choice of the 2-(*N*-cyclohexylimino)-1,3-diphenylpropane system in dimethyl sulfoxide-d_6 for the study of the imine–enamine tautomerism appears to be a rather fortunate one. The observation that all of the equilibrium constants for the chemical processes involved are rather close to unity allows the rather precise measurement of the relative concentrations of all three of the species present and hence of the corresponding equilibrium constants and thermodynamic quantities by the simple but relatively insensitive variable temperature nmr method. Although it would appear that this method is, *in lieu* of further refinements, restricted to those systems for which the value of the equilibrium constants to be determined is neither appreciably smaller than 0.1 nor greater than 10, the simplicity and ease of application of the method make it extremely attractive for those systems to which it is applicable.

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 δ 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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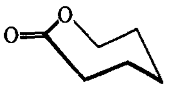
Abstract: Fluorine magnetic resonance spectroscopy has been used to determine the rates of ring inversion of γ,γ-difluoro-ε-caprolactone and γ,γ-difluoro-ε-caprolactam. Free energies of activation of 10.0 and 10.4 kcal/mol at −53° were found for the lactone and lactam, respectively. The nmr spectra for 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 for a planar lactone function.[8] Pseudorotation of the



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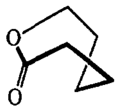

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(2) National Science Foundation Summer Fellow, 1966 and 1968; National Defense Education Act Trainee, 1968–1969.

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(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]

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