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# Relative Thermodynamic Stabilities of γ-Methylene-γ-butyrolactone and α-Angelicalactone

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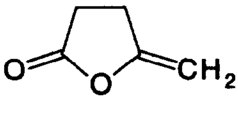
***Abstract:*** The relative thermodynamic stabilities of the title compounds have been determined by chemical equilibration in cyclohexane and dipentyl ether solutions at several temperatures. In each solvent, α-angelicalactone is favored thermodynamically, the values of $\Delta H^{\circ}$ and $\Delta S^{\circ}$ being ca. -8.0 kJ $mol^{-1}$ and 2 J $K^{-1}$ $mol^{-1}$, respectively, for the γ-methylene-γ-butyrolactone → α-angelicalactone isomerization.

The isomeric lactones, 5-methylene-dihydro-2(3*H*)-furanone **1** and 5-methyl-2(3*H*)-furanone **2** (γ-methylene-γ-butyrolactone and α-angelicalactone, respectively), are structurally related to the 5-membered cyclic vinyl ethers 2-methylenetetrahydrofuran **3** and 5-methyl-2,3-dihydrofuran **4**. The latter two compounds have been studied in our laboratory, with the purpose of clarifying the kinetics of their hydrolysis and determination of their relative thermodynamic stabilities.[1] Thus, in diethyl ether solution the values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the **3** → **4** reaction were found to be -4.7 ± 0.3 kJ $mol^{-1}$ and 8.0 ± 1.0 J $K^{-1}$ $mol^{-1}$, respectively, *i.e.* the endocyclic form (**4**) is favored by both the enthalpy and entropy terms.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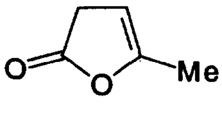
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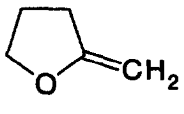
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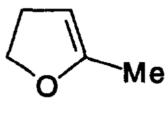
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Vinyl ethers like 3 and 4 are characterized by p-π conjugation between the lone pair electrons of the O atom and π electrons of the C=C bond:

$$-O-C=C \leftrightarrow -\overset{+}{O}= C-\overset{-}{C}$$

In the lactones 1 and 2, the ethereal O atom may additionally conjugate with the neighboring C=O group; moreover, the heterocyclic ring of these lactones has an additional trigonally hybridized C atom, relative to that of the corresponding vinyl ethers. These obvious structural differences between the two pairs of isomers have an unpredictable effect on molecular stability, which justified a determination of the relative thermodynamic stabilities of the title lactones by chemical equilibration. No previous thermodynamic study of 1 and 2 has been published; however, it has been found that in the presence of an acid catalyst 1 is isomerized to 2 in high yield.[2]

## RESULTS AND DISCUSSION

The isomerization of 3 to 4 was studied in two solvents, cyclohexane and dipentyl ether, with iodine as catalyst in the hydrocarbon solvent and p-toluenesulfonic acid in the ether. In dipentyl ether, the attainment of thermodynamic equilibrium was more straightforward, which is reflected in the smaller errors of the thermodynamic parameters of isomerization. The values of the experimental equilibrium constant at different temperatures, and the calculated thermodynamic parameters $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ at 298.15 K, obtained from the van't Hoff equation, are given in Table 1.

Within experimental error, the values of the thermodynamic parameters of isomerization may be considered equal for the two solvents used. In comparison with the reaction 3 → 4, the isomerization of 1 to 2 is more exothermic by 3-4 kJ $\text{mol}^{-1}$; thus the additional *sp*$^2$ hybridized C atom in the lactone ring and the possibility of conjugation with the C=O group has the effect of decreasing the relative (thermochemical) stability of the exocyclic isomer. On the other hand, the endocyclic lactone 4 is less favored by the entropy term than the corresponding vinyl ether 2. The markedly different reaction entropies in the apparently similar structural changes have a simple explanation if it is assumed that the 5-membered ring of 2 is fully planar whereas that of 4 is nonplanar with C-2 on either side of the ring: in that case the latter compound is statistically favored over 2 by a factor of 2. (Both of the exocyclic compounds 1 and 3 probably have nonplanar skeletons, and hence do not differ statistically). Indeed, it has been shown by

**Table 1.** Values of the Equilibrium Constant K(2/1) at Different Temperatures, Together with the Thermodynamic Parameters.[a]

| | Temperature/°C | | | | | | |
|---|---|---|---|---|---|---|---|
| Solvent | 25 | 50 | 75 | 100 | 125.0 | 150 | 170 |
| Cyclohexane | 37.5 | 29.2 | 20.7 | 17.9 | 16.4 | 13.4 | |
| Dipentyl ether | 33.1 | 25.5 | 20.6 | 18.5 | 15.1 | 13.0 | 11.3 |

Values of the Thermodynamic Parameters at 298.15 K for 1 → 2:

| Solvent | $\Delta G^\circ$/kJ mol$^{-1}$ | $\Delta H^\circ$/kJ mol$^{-1}$ | $\Delta S^\circ$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| Cyclohexane | -8.94 ± 0.21 | -8.5 ± 1.1 | 1.4 ± 3.1 |
| Dipentyl ether | -8.68 ± 0.12 | -7.9 ± 0.6 | 2.7 ± 1.5 |

[a]The errors are twice the standard errors of a linear regression of lnK *vs.* $T^{-1}$

MW spectroscopy that compound **2** really is planar in the ground state,[3] whereas **4** has a bent ring with the C-2 atom out of the plane formed by the other heavy atoms.[4] Accordingly, the difference in the statistical factors causes reaction **1** → **2** to have a lower entropy by Rln2 = 5.8 J $K^{-1}$ $mol^{-1}$, which agrees with the experimental data.

## EXPERIMENTAL

*Materials.* The two lactones were commercial products from Aldrich Co.

*Equilibrium experiments.* In both solvents, substrate concentration was maintained at 10 vol-%. The cyclohexane solution was 0.01M in $I_2$, and the dipentyl ether solution contained 1 mg p-TsOH/ml. The position of equilibrium was approached from both directions. At each temperature, the values of the mean equilibrium constant are based on 6 to 11 determinations. Equilibration times varied from an hour to several weeks at the lowest temperatures used. Prior to GLC analysis of the equilibrated samples by a 50 m capillary column of type Silar 9C, the catalyst was destroyed by addition of an excess of diethylamine. More details of the experimental procedure may be found from Ref. 5.

## REFERENCES

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