# Thermodynamics of Vinyl Ethers. IX.* The Relative Stabilities of 4-Methylene-1,3-dioxane and 4-Methyl-1,3-dioxene-(4)

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Equilibrium concentrations of the title compounds in cyclohexane solution at various temperatures have been determined. The following results were obtained for the isomerization of 4-methylene-1,3-dioxane to 4-methyl-1,3-dioxene-(4) at 298.15 K: $\Delta G° = -19.9 \pm 0.2$ kJ mol^{-1}, $\Delta H° = -16.1 \pm 0.8$ kJ mol^{-1} and $\Delta S° = 12.8 \pm 2.3$ J K^{-1} mol^{-1}. In the gas phase at 298.15 K, the values of $\Delta H°$ and $\Delta S°$ were obtained as -18.3 ± 0.9 kJ mol^{-1} and 10.2 ± 2.4 J K^{-1} mol^{-1}, respectively.

In a recent work by this author,[1] thermodynamics of the exo→endo isomerization of a number of five- and six-membered unsaturated heterocyclic ethers, such as 2-methylenetetrahydropyran (I) and 6-methyl-3,4-dihydro-2H-pyran (II), were investigated. In diethyl ether
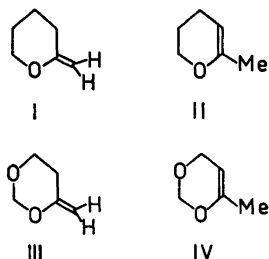
Scheme 1.

solution at 298.15 K, the standard Gibbs free energy change for I→II was obtained to be -21.8 kJ mol^{-1}. The corresponding value for the isomerization of 4-methylene-1,3-dioxane (III) to 4-methyl-1,3-dioxene-(4) (IV) has been reported to be about -12.2 kJ mol^{-1},[2] which

appeared amazing, since it is difficult to see any factor which could give rise to such a large difference between the values of $\Delta G°$ for the two similar isomerization reactions. Hence it was considered necessary to make a reinvestigation of the relative stabilities of III and IV.

EXPERIMENTAL

4-Chloromethyl-1,3-dioxane was prepared from paraformaldehyde (200 g), allyl chloride (320 cm³) and concentrated sulfuric acid (120 cm³) as described by Price and Krishnamutri.[3] The yield was 90 g (17 %), boiling temperature 352 to 356 K at 2.1 kPa. The product was distilled from an excess of potassium hydroxide to give a mixture of water and III, which was collected over potassium carbonate. The organic layer was separated, dried (K₂CO₃), and distilled. The yield of III, boiling temperature 337 to 338 K at 15.6 kPa, was 55 %. The product was converted into IV (boiling temperature 381 K at 101.3 kPa) by slow distillation at atmospheric pressure.

The *NMR spectra* were taken in CCl₄ solution with TMS as internal standard. III: τ 5.05 (O−CH₂−O), 6.13 (O−CH₂−C), 7.77 (C−CH₂−C), 5.60 (H trans to O), 5.42 (H cis to O); IV: τ 5.05 (O−CH₂−O), 5.87 (O−CH₂−C), 5.87 (C=C−H), 8.26 (CH₃).

Determination of normal boiling temperatures.[4] Reference curve (compound, normal b.t., relative retention time): isobutylidene ethyl ether, 366.7 K, 0.312; 1-methoxycyclopentene, 387.0 K, 0.511; 1-methoxycyclohexene, 417.1 K, 1.000. The relative retention times of III and IV were 0.597 and 0.443, respectively, corresponding to normal boiling temperatures of about 395.0 (III) and 380.9 K (IV).

Procedure. The equilibrations were carried out in cyclohexane with iodine as catalyst. Substrate concentration was about 4 mol dm^{-3} and catalyst concentration 0.01 mol dm^{-3}. Two initial mixtures were available for the equilibra-

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tions: "pure" III and "pure" IV; although the concentration of III in the latter was less than 1 %, it exceeded the equilibrium concentration of III, and hence the position of equilibrium was always approached from the side of the *exo* isomer (III). To be sure that the true equilibrium had been achieved, the progress of isomerization was followed over sufficiently extended periods of time (several times the time necessary for the isomer ratio to become constant). The column used in the gaschromatographic analyses was an 8 m column containing 10 % Carbowax 20 M on Chromosorb G. The compounds were eluted in the order IV, III. After the first isomer had been eluted through the column, the attenuation of the detector was decreased by a nominal factor of 250 to get a peak of detectable size for the less stable isomer (III). The real change of attenuation was found to be 218 ± 2 by a procedure described previously.[1] The relative peak areas were determined by the cut-and-weigh method, and the area ratio, A_{IV}/A_{III}, was multiplied by 218 to get the true mol ratio at equilibrium. The practical performance of the equilibrations has been described in more detail previously.[4]

RESULTS

Table 1 shows the values of the mean equilibrium constant K and its standard error at various temperatures. The values of the thermodynamic functions of isomerization at 298.15 K were obtained by a linear least-squares treatment of $\Delta G°$ against temperature T. The results are: $\Delta G° = -19.9 \pm 0.2$ kJ mol^{-1}, $\Delta H° = -16.1 \pm 0.8$ kJ mol^{-1} and $\Delta S° = 12.8 \pm 2.3$ J K^{-1} mol^{-1} for the isomerization of III to

Table 1. Values of the mean equilibrium constant K and its standard error for the reaction 4-methylene-1,3-dioxolane $\rightleftharpoons$ 4-methyl-1,3-dioxene-(4) in cyclohexane solution at various temperatures; n denotes the number of independent determinations.

T/K	n	K (endo/exo)
282.2	2	4160 ± 260
298.2	5	3060 ± 130
316.2	3	2130 ± 90
326.2	2	1860 ± 100
336.2	2	1540 ± 70
358.2	3	932 ± 52
375.2	3	777 ± 27
391.2	3	680 ± 23
399.2	2	578 ± 20
413.2	2	507 ± 7

IV in cyclohexane solution at 298.15 K (the errors are twice the standard errors). The values of $\Delta H°(g)$ and $\Delta S°(g)$ were evaluated to be -18.3 ± 0.9 kJ mol^{-1} and 10.2 ± 2.4 J K^{-1} mol^{-1}, respectively, from the liquid phase data and the normal boiling temperatures.[4]

DISCUSSION

According to the results of this study, the difference (-19.9 kJ mol^{-1}) in the standard Gibbs free energy between IV and III is close to that (-21.8 kJ mol^{-1}, Ref. 1) between II and I. Interestingly, the corresponding difference between 1-methylcyclohexene (VI) and methylenecyclohexane (V) is -13.2 kJ mol^{-1}.[5] Herling *et al.*[5] have shown that the value of $\Delta S°(g)$ in V→VI is about 13 J K^{-1} mol^{-1}, which, within experimental error, is equal to that in III→IV, 10.2 ± 2.4 J K^{-1} mol^{-1}. The value of $\Delta S°(l)$ in diethyl ether for I=II has been obtained to be 28 ± 13 J K^{-1} mol^{-1} (the error quoted here is twice the standard error),[1] but it is evident that the high value of $\Delta S°$ in the latter case is due to solvation, since the values of $\Delta S°$ for other similar reactions studied in the same work[1] were considerably less positive if hexane was used as solvent in the equilibrations (for instance, $\Delta S°(l)$ for (Z)-2-ethylidenetetrahydropyran → 6-ethyl-3,4-dihydro-2H-pyran was obtained to be about 17 J K^{-1} mol^{-1} in diethyl ether but only about 9 J K^{-1} mol^{-1} in hexane). Thus it is likely that the entropy changes in the reactions I→II, III→IV, and V→VI are quite similar, and the differences in the values of $\Delta G°$ are due to enthalpy differences. It is remarkable that the difference in the standard Gibbs free energy between V and VI is *smaller* than that between I and II (or between III and IV). In the case of the five-membered analogues of V and VI, methylenecyclopentane and 1-methylcyclopentene, respectively, the value of $\Delta G°(l, 298.15$ K) in *exo→endo* is -17.3 kJ mol^{-1},[5] while that for the reaction between the five-membered analogues of I and II, 2-methylenetetrahydrofuran and 5-methyl-2,3-dihydrofuran, respectively, is -7.1 kJ mol^{-1}.[1] The latter result is "natural" in the sense that on going from *exo* to *endo*, the number of alkyl groups attached to the double bond increases by one, and since alkyl groups do not stabilize the double bond of a

vinyl ether as effectively as they do an "ordinary" olefinic double bond,[1,6] the value of $\Delta G°$ (and that of $\Delta H°$, too, since entropy changes are be similar in both reactions) ought to be less negative in the latter reaction, in accord with experiment. Clearly, the situation is more complicated in the six-membered ring compounds. In a previous study,[1] the low thermodynamic stability of the exo-cyclic member of the exo-endo pair, I and II, was assumed to be due to an unfavorable orientation of the p-orbitals of the lone-pair electrons of the oxygen atom for an effective conjugation with the π-orbital of the double bond in the exo-cyclic isomer (I), which was assumed to have a chair conformation. Support for decreased conjugation in the exo compounds I and III is obtained from their NMR spectra: in most acyclic alkyl vinyl ethers, the chemical shifts of the terminal hydrogen atoms of the vinyl group are located about 1 ppm upfield from the corresponding shifts in simple olefins, or at about τ 6.2. On the other hand, the hydrogen atoms of the exo-cyclic methylene groups of I and III absorb at about τ 5.9 (Ref. 1) and τ 5.5, respectively. For comparison, the corresponding signals of 2-methylenetetrahydrofuran and 4-methylene-1,3-dioxolane are found at τ 6.1 (Ref. 1) and τ 5.9,[7] respectively. Hence the lower τ-values of the signals due to the protons of the exo-cyclic methylene group in the six-membered heterocycles indicate increased double-bond character of the ethylenic linkage resulting from the reduced resonance interaction between the lone-pair electrons of the oxygen atom and the π-electrons of the double bond.[8-10]
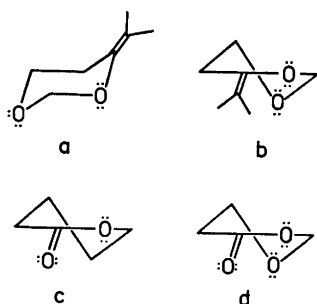
The chair conformation (a) is not the only imaginable conformation for III (and for I), since it is possible that an energetically more favorable spatial structure might be the half-chair conformation (b), where effective conjugation between the lone-pair electrons and π-electrons seems more likely. This aspect is in accordance with the probable conformations of unsubstituted δ-lactones (c) and 4-oxo-1,3-dioxanes (d),[11-13] but as stated above, the NMR shift data suggest that conjugation is weak in the exo forms I and III, which is best interpretable in terms of the chair structure.

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Scheme 2.