Thermodynamics of Vinyl Ethers. XII.* The Relative Stabilities of 2-Alkylidenetetrahydrofurans and 5-Alkyl-2,3-dihydrofurans

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The relative stabilities of 2-alkylidenetetrahydrofurans and their *endo*-cyclic isomers, 5-alkyl-2,3-dihydrofurans (alkyl = Et, i-Pr, i-Bu) have been determined by chemical equilibration in cyclohexane solution. At 298.15 K, the *endo*cyclic compounds are thermodynamically more stable than their *exo*-cyclic isomers except for the case alkyl = i-Pr. Of the two geometric isomers of 2-ethylidenetetrahydrofuran and 2-isobutylidenetetrahydrofuran, the *Z* form (with Me or i-Pr *cis* to ring oxygen) is the more stable one. The standard entropy change in each *exo→endo* isomerization is positive; comparison of the value of $\Delta S°$ for alkyl = Et with that for alkyl = i-Bu suggests that the rotation of the i-Pr group about the $C-C(sp^2)$ bond in 2-isobutylidenetetrahydrofuran is hindered by the proximity of the ring atoms.

The relative stabilities of 2-alkylidenetetrahydrofurans and 5-alkyl-2,3-dihydrofurans, and of 2-alkylidenetetrahydropyrans and 6-alkyl-3,4-dihydro-2H-pyrans were treated in a recent study by the present author.[1] The isomeric compounds were equilibrated in diethyl ether solution with p-toluenesulfonic acid as catalyst, and their relative concentrations at equilibrium were determined by GLC. When the experimental work was practically completed, Rhoads *et al.*[2] reported that iodine in an inert solvent had been found to be a good catalyst-solvent combination for equilibration experiments on α,β-unsaturated ethers. To test the applicability of this method for equilibration of the heterocyclic ethers concerned, a few of the six-membered *exo-endo* pairs were equilibrated in hexane

with iodine as catalyst. The values of $\Delta H°$ and $\Delta S°$ of isomerization were found to differ considerably from those obtained by using diethyl ether as solvent. In a later study however,[3] the effect of solvent on the equilibrium between the acyclic compounds 2-methoxy-3-methyl-1-butene and 2-methoxy-3-methyl-2-butene was found to be small. In view of these opposing results it was considered necessary to make a reinvestigation of the relative stabilities of the five-membered heterocyclic ethers concerned, now in an inert solvent. Besides for the clarification of the solvent effect, the study was justified by a need of "basic" thermodynamic data of isomerization, relevant to an inert solvent, for these simple heterocyclic ethers for comparative purposes in some future investigations dealing with more complex unsaturated ethers. Thus the compounds II—IV were prepared (compound III was not included in the previous study [1]) and the thermodynamics

$$(1)$$
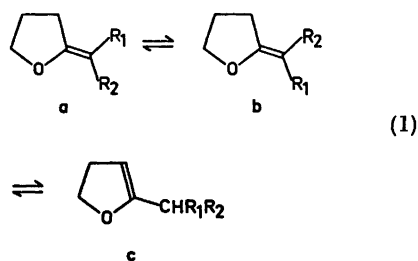
I: $R_1=R_2=H$ (Ia≡Ib). III: R_1=i-Pr, R_2=H.
II: R_1=Me, R_2=H. IV: $R_1=R_2$=Me
(IVa≡IVb).

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Table 1. Thermodynamic data for the reactions quoted in eqn. 1 in the liquid phase at 298.15 K. The errors are twice the standard errors.

Reaction	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
IIa→IIc[a]	-3.99 ± 0.03	-1.9 ± 0.2	7.0 ± 0.4
IIIa→IIIc[b]	-6.56 ± 0.08	-3.0 ± 0.5	12.0 ± 1.5
IVa→IVc[c]	4.60 ± 0.05	6.3 ± 0.3	5.6 ± 0.7
IIb→IIc[a]	-0.44 ± 0.04	1.9 ± 0.2	7.7 ± 0.7
IIIb→IIIc[b]	-3.13 ± 0.04	-0.1 ± 0.3	10.2 ± 0.7
IIa→IIb[a]	-3.54 ± 0.04	-3.8 ± 0.2	-0.7 ± 0.7
IIIa→IIIb[b]	-3.42 ± 0.05	-2.9 ± 0.3	1.9 ± 0.9

[a] The reaction was studied between 282 and 403 K. [b] Studied between 282 and 400 K. [c] Studied between 282 and 428 K.

Table 2. Thermodynamic data for the reactions quoted in eqn. 1 in the gas phase at 298.15 K.

Reaction	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
IIa→IIc	-5.0 ± 0.4	3.5 ± 0.6
IIIa→IIIc	-5.9 ± 0.6	8.9 ± 1.6
IVa→IVc	2.6 ± 0.4	1.7 ± 0.9
IIb→IIc	-0.1 ± 0.4	5.4 ± 0.9
IIIb→IIIc	-2.0 ± 0.4	8.2 ± 0.9
IIa→IIb	-4.8 ± 0.4	-1.9 ± 0.9
IIIa→IIIb	-3.9 ± 0.4	0.8 ± 1.0

of their isomeric interconversion was studied. As it turned out that the effect of solvent on the values of the thermodynamic parameters was negligible, investigation of reaction Ia⇌Ic was not repeated, since analysis of the equilibrium mixtures of Ia and Ic by GLC is laborious, due to the easy isomerization of Ia to Ic.

EXPERIMENTAL

Materials. The following synthetic route was employed:[1] ClCH$_2$CH$_2$CH$_2$COCl → ClCH$_2$CH$_2$CH$_2$COCHR$_1$R$_2$ $\xrightarrow{\Delta}$ HOCH$_2$CH$_2$CH$_2$COCHR$_1$R$_2$ → a,b,c. The chloro ketones were now prepared from 4-chlorobutyryl chloride and the appropriate organomagnesium halide (instead of the corresponding organozinc halide[4]) by the method suggested by Cason and Kraus[5] for the preparation of aliphatic ketones. The yields and boiling temperatures of the ketones prepared were: R$_1$=Me, R$_2$=H: 42 %, b.t. 334.7 K at 0.8 kPa (lit.[1] 39 %, b.t. 348 to 358 K at 1.6 to 2.1 kPa); R$_1$=i-Pr, R$_2$=H: 65 %, b.t. 358 K at 1.1 kPa; R$_1$=R$_2$=Me: 45 %, b.t. 348 to 350 K at 1.5 kPa (lit.[1] 12 %, b.t. 356 to 357 K at 2.1 kPa). The physical constants of I, II, and IV

have been published previously.[1] IIIc: b.t. 338 K at 6.0 kPa. *NMR* (60 MHz, CCl$_4$, TMS): I, II, and IV, see Ref. 1; IIIc: τ 5.78 (CH$_2$-O), 7.45 (C-CH$_2$-C in the ring), 5.53 (=C—H), 8.09 (CH$_2$ in the side chain), 9.08 (CH$_3$), the signal of the methine proton of the i-Bu group was not detected; J_{vic} (CH$_2$-CH$_2$) 9.5 Hz, J_{vic} (CH$_2$—CH=) 2.0 Hz. The *normal boiling temperatures* of the isomeric vinyl ethers studied were determined by the method described previously.[6] IIa, 401.8 K; IIb, 395.2 K; IIc, 382.7 K; IIIa, 433.0 K; IIIb, 426.7 K; IIIc, 414.8 K; IVa, 417.4 K; IVc, 394.6 K.

Procedure. The equilibrations were carried out in cyclohexane with iodine as catalyst.[2,3]

RESULTS

The values of the thermodynamic parameters of isomerization in the liquid phase at 298.15 K are shown in Table 1, and the values of $\Delta H°$(g) and $\Delta S°$(g) at 298.15 K, evaluated from the liquid phase data and the normal boiling temperatures,[6] in Table 2.

DISCUSSION

The change of solvent from diethyl ether to cyclohexane has no practical effect on the values of the thermodynamic functions of isomerization as can be seen from the following examples (the errors are twice the standard errors):

Reaction	Solvent	$\Delta H°$/ kJmol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
IIa→IIb	Et$_2$O (Ref. 1)	-3.7 ± 0.7	-1.6 ± 2.6
	C$_6$H$_{12}$	-3.8 ± 0.2	-0.7 ± 0.7
IIb→IIc	Et$_2$O (Ref. 1)	2.0 ± 0.5	8.0 ± 2.0
	C$_6$H$_{12}$	1.9 ± 0.2	7.7 ± 0.7
IVa→IVc	Et$_2$O (Ref. 1)	6.4 ± 0.5	5.5 ± 1.8
	C$_6$H$_{12}$	6.3 ± 0.3	5.6 ± 0.7

Thus it is reasonable to assume that the values of $\Delta H^{\circ}(l)$ and $\Delta S^{\circ}(l)$ (-4.7 ± 0.6 kJ mol^{-1} and 8.0 ± 2.0 J K^{-1} mol^{-1},[1] respectively, the errors being twice the standard errors) for reaction Ia→Ic in diethyl ether solution should, within experimental error, correspond to those obtainable from experiments performed in an inert solvent, such as cyclohexane. In the gas phase therefore, the values of ΔH° and ΔS° for Ia→Ic should be about -7.8 kJ mol^{-1} and 4.2 J K^{-1} mol^{-1},[7] since the normal boiling temperatures of Ia and Ic are about 373 and 354 K,[1] respectively.

The conclusions extractable from the values of the changes of the thermodynamic parameters for reactions involving the isomeric forms of I, II, and IV have been discussed in detail previously,[1] but some essential features will be briefly treated here together with new findings on the basis of gas-phase data, unavailable in the previous study.
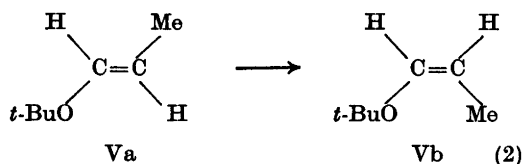
The relative stability of the *exo* isomers (a,b) increases with increasing number of alkyl groups attached to the double bond of the *exo* form. For example, the values of $\Delta H^{\circ}(g)$ for Ia→Ic and IIa→IIc are -7.8 and -5.0 kJ mol^{-1}; the methyl group of IIa thus stabilizes the double bond by about 3 kJ mol^{-1}. For comparison, the standard enthalpies of isomerization of methylenecyclopentane to 1-methylcyclopentene and of ethylidenecyclopentane to

1-ethylcyclopentene are about -16 and -5 kJ mol^{-1}, respectively, in acetic acid solution.[7] Hence the methyl group of ethylidenecyclopentane stabilizes the double bond by about 11 kJ mol^{-1}. Possible reasons for the weak stabilizing effect of alkyl groups on the double bond of vinyl ethers have been suggested previously.[1,3] The same phenomenon seems to be responsible for the fact that the value of $\Delta H^{\circ}(g)$ for Ia→Ic (-7.8 kJ mol^{-1}) is about 8 kJ mol^{-1} less negative than that for methylenecyclopentane → 1-methylcyclopentene, *i.e.* about -16 kJ mol^{-1} (since the normal boiling temperatures of the two olefins concerned are equal within 1 K,[8,9] the values of $\Delta H^{\circ}(l)$ and $\Delta H^{\circ}(g)$ for the latter reaction should be practically equal, see Ref. 6). In each *exo→endo* reaction in question, the number of alkyl substituents attached to the double bond increases by one, and since the stabilization due to a single alkyl group should be about 11 kJ mol^{-1} in olefins (*cf.* ethylidenecyclopentane above), but only 3 kJ mol^{-1} in vinyl ethers, the value of $\Delta H^{\circ}(g)$ in Ia→Ic might be expected to be about $-16+(11-3)=-8$ kJ mol^{-1}, which agrees well with the experimental value of about -7.8 kJ mol^{-1}.

The values of $\Delta H^{\circ}(g)$ and $\Delta S^{\circ}(g)$ for IIa→IIb are interesting in comparison with those for reaction (2), for which $\Delta H^{\circ}(g)=-2.9\pm0.3$ kJ
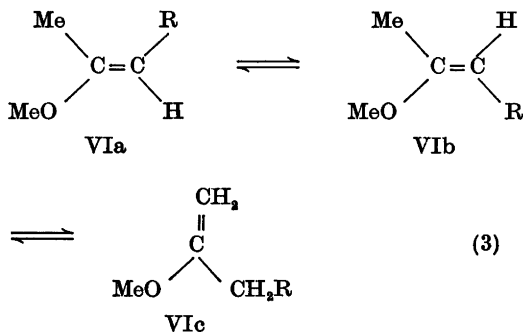
Table 3. Experimental data for reactions (1) and (3). The data for reaction (3) are from Ref. 12. Gas phase, 298.15 K.

Reaction		$\Delta H^{\circ}(g)$/kJ mol^{-1}	$\Delta S^{\circ}(g)$/J K^{-1} mol^{-1}
IIIa→IIIc		$-5.9(\pm0.6)$	$8.9(\pm1.6)$
IIa→IIc		$-5.0(\pm0.4)$	$3.5(\pm0.6)$
	$\Delta=$ -0.9		$\Delta\cong$ 5
VIa→VIc,	R$=$i-Pr	$-0.6(\pm0.4)$	$6.4(\pm0.8)$
	R$=$Me	$-0.5(\pm0.4)$	$1.6(\pm0.8)$
	$\Delta=$ -0.1		$\Delta\cong$ 5
IIIb→IIIc		$-2.0(\pm0.4)$	$8.2(\pm0.9)$
IIb→IIc		$-0.1(\pm0.4)$	$5.4(\pm0.9)$
	$\Delta=$ -1.9		$\Delta\cong$ 3
VIb→VIc,	R$=$i-Pr	$-12.2(\pm0.4)$	$-9.1(\pm0.9)$
	R$=$Me	$-10.3(\pm0.6)$	$-11.8(\pm1.5)$
	$\Delta=$ -1.9		$\Delta\cong$ 3

$$\underset{\text{Va}}{\overset{t\text{-BuO}}{\underset{}{}}}\text{C=C}\overset{\text{H}}{\underset{\text{H}}{}} \longrightarrow \underset{\text{Vb}}{\overset{t\text{-BuO}}{\underset{}{}}}\text{C=C}\overset{\text{H}}{\underset{\text{Me}}{}} \quad (2)$$

mol^{-1} and $\Delta S°(g)=5.3\pm0.6$ J K^{-1} mol^{-1}.[10] The enthalpy change in IIa→IIb is about 2 kJ mol^{-1} more negative than that in reaction (2). Since it seems unlikely that the difference, at least totally, could be ascribed to steric repulsions between the methyl group and ring hydrogens in IIa (the corresponding strain is less than 1 kJ mol^{-1} in the analogous compound ethylidene-cyclopentane [11]), it is possible that attractive forces between the methyl group and oxygen atom are more pronounced in IIb than in Vb. Inspection of molecular models shows that the shape of the five-membered ring in IIb leads to a slightly increased distance, relative to that in Vb, between the methyl group and oxygen atom, which appears to be advantageous for enhanced stability.

Some of the results of the present work are compared with data for reaction (3) in Table 3. The enthalpy data show that the *cis*

$$\underset{\text{VIa}}{\overset{\text{Me}}{\underset{\text{MeO}}{}}}\text{C=C}\overset{\text{R}}{\underset{\text{H}}{}} \rightleftharpoons \underset{\text{VIb}}{\overset{\text{Me}}{\underset{\text{MeO}}{}}}\text{C=C}\overset{\text{H}}{\underset{\text{R}}{}}$$

$$\rightleftharpoons \underset{\text{VIc}}{\overset{\text{CH}_2}{\underset{\text{MeO}}{}}}\overset{\parallel}{\underset{}{\text{C}}}\overset{}{\underset{\text{CH}_2\text{R}}{}} \quad (3)$$

interaction between Me and R in VIa is the same for R=Me and R=i-Pr. The data also suggest that the corresponding interaction in IIIa might be slightly greater than that in IIa, although the values of $\Delta H°(g)$ for IIIa→IIIc and IIa→IIc are, in fact, equal if the experimental uncertainty in the values of $\Delta H°(g)$ is taken into account. However, the stabilizing *cis* interaction between MeO and R in VIb is definitely greater (by about 1.9 kJ mol^{-1}) for R=Me than for R=i-Pr. This result is confirmed by enthalpy data for IIIb→IIIc and IIb→IIc.

The value of $\Delta S°(g)$ for IIIa→IIIc is about 5 J K^{-1} mol^{-1} more positive than that for IIa→IIc; this compares well with the difference in the corresponding values for reaction VIa→VIc in cases R=i-Pr and R=Me. On the other hand, the difference in the values of $\Delta S°(g)$ for IIIb→IIIc and IIb→IIc is 3 J K^{-1} mol^{-1}, which is the same as the corresponding difference for reaction VIb→VIc in cases R=i-Pr and R=Me. These results probably show that rotation of the i-Pr group about the C(sp^3)—C(sp^2) bond in, for instance, IIIa is restricted by the *cis* substituent (ring hydrogens in IIIa), which decreases the entropy of the *a* isomer relative to that of the *c* isomer, where the i-Pr group should be free to rotate.

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