

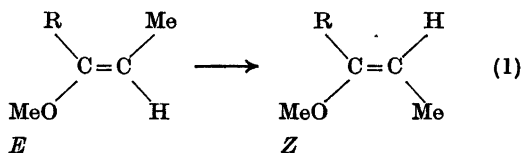
Thermodynamics of Vinyl Ethers. XIV.* Effect of Aromatic and Heteroaromatic α -Substituents on the Relative Stabilities of Geometric Isomers

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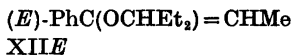
The thermodynamics of *cis-trans* isomerization in vinyl ethers of the type $\text{RC}(\text{OR}')=\text{CHMe}$, where R is an aromatic or a heteroaromatic substituent and $\text{R}'=\text{Me}$ or Et_2CH , have been studied by chemical equilibration. For $\text{R}=\text{Ph}$ and $\text{R}'=\text{Me}$, $\Delta G^\ominus = -1.60 \pm 0.06 \text{ kJ mol}^{-1}$, $\Delta H^\ominus = 1.8 \pm 0.8 \text{ kJ mol}^{-1}$ and $\Delta S^\ominus = 11.5 \pm 2.5 \text{ J K}^{-1} \text{ mol}^{-1}$ for the $E \rightarrow Z$ isomerization in cyclohexane solution at 298.15 K. Substituents in the phenyl group can significantly alter the relative stability of the E, Z pair only if they are in the *ortho*-position, the stability of the E isomer being favored by *ortho*-substituents. 2-Furyl and 2-thienyl groups are practically equivalent to a phenyl group as the α -substituent. Bulky alkoxy groups favor the relative stability of the Z isomer.

The present paper describes the results of a study of the effect of aromatic and heteroaromatic α -substituents (R) on the thermodynamics of reaction (1). In addition, the effect of the size of the alkoxy group was clarified by the reaction (2).



I: $\text{R}=\text{C}_6\text{H}_5$ (phenyl); II: $\text{R}=\textit{p}\text{-Me}-\text{C}_6\text{H}_4$; III: $\text{R}=\textit{p}\text{-MeO}-\text{C}_6\text{H}_4$; IV: $\text{R}=\textit{p}\text{-Cl}-\text{C}_6\text{H}_4$; V: $\text{R}=\textit{p}\text{-F}-\text{C}_6\text{H}_4$; VI: $\text{R}=\textit{m}\text{-Me}-\text{C}_6\text{H}_4$; VII: $\text{R}=\textit{o}\text{-Me}-\text{C}_6\text{H}_4$; VIII: $\text{R}=\textit{o}\text{-MeO}-\text{C}_6\text{H}_4$; IX: $\text{R}=\textit{o}\text{-Cl}-\text{C}_6\text{H}_4$; X: $\text{R}=\text{C}_4\text{H}_3\text{O}$ (2-furyl); XI: $\text{R}=\text{C}_4\text{H}_2\text{S}$ (2-thienyl).

* Part XIII: Taskinen, E. and Jokila, K. *Acta Chem. Scand. B* 29 (1975) 249.



EXPERIMENTAL

Materials. The vinyl ethers were prepared from the appropriate ketones *via* the route $\text{R}^1\text{R}^2\text{CO} \rightarrow \text{R}^1\text{R}^2\text{C}(\text{OMe})_2 \rightarrow$ a vinyl ether (e.g. propiophenone \rightarrow propiophenone dimethyl acetal \rightarrow 1-methoxy-1-phenylpropene) as illustrated in the previous parts of this series. The ketones, unless commercially available, were prepared by conventional methods. The vinyl ethers were isolated as mixtures of the two geometric isomers with an $E:Z$ ratio of about 0.5 for I-VI, X, XI, 2 for VII-IX, and 0.3 for XII. The following boiling temperatures were observed during final distillation: I 478 to 479 K at 100.0 kPa; II 496 to 501 K at 101.3 kPa; III 410 to 417 K at 2.5 kPa; IV 400 to 401 K at 2.1 kPa; V 355 to 356 K at 1.2 kPa; VI 366 to 367 K at 1.1 kPa; VII 355 K at 1.2 kPa; VIII 380 to 381 K at 1.3 kPa; IX 369 to 372 K at 1.2 kPa; X 331 to 340 K at 1.3 kPa; XI 360 to 363 K at 1.5 kPa; XII about 393 K at 1.3 kPa (the compound was prepared from I and 3-pentanol by transesterification, for examples see Ref. 1). If necessary, the synthetic products were purified by preparative GLC, but isolation of the pure isomers in preparative scale was too laborious due to their similar retention times (exception: I). *NMR spectra.* The δ values (CCl_4 , TMS) of some characteristic peaks are given in Table 1.

Equilibrations. The equilibrations were carried out at about five temperatures from about 300 to 405 K (298 to 373 K for XII) with cyclohexane as solvent and iodine as catalyst (see previous papers of this series). The total number of independent determinations varied

Table 1. NMR shift data (δ values, CCl_4 , TMS) for some characteristic peaks of the compounds studied in this work.

Com- pound	MeO		β -Me		Olefinic proton	
	<i>E</i>	<i>Z</i>	<i>E</i>	<i>Z</i>	<i>E</i>	<i>Z</i>
I	3.52	3.43	1.64	1.73	4.65	5.18
II	3.51	3.42	1.64	1.71	4.63	5.15
III	3.51	3.42	1.65	1.71	4.59	5.08
IV	3.54	3.44	1.64	1.73	4.68	5.23
V	3.54	3.44	1.64	1.74	4.67	5.18
VI	3.52	3.44	1.64	1.73	4.66	5.21
VII	3.50	3.22	1.40	1.70	4.69	4.64
VIII	3.51	3.31	1.40	1.71	4.68	4.91
IX	3.54	3.31	1.41	1.74	4.74	4.80
X	3.54	3.59	1.87	1.73	4.74	5.41
XI	3.56	3.56	1.82	1.70	4.74	5.25
XII	? ^a	1.71	4.83	5.06

^a Obscured by other signals.

from 20 to 40. The equilibrated samples were analyzed by GLC. This method, however, was not applicable to XII, since the isomers had practically identical retention times. Thus the samples were analyzed by NMR from the relative integrated intensities of the signals at δ 4.83 (*E*) and 5.06 (*Z*).

CONFIGURATIONAL ASSIGNMENT

Configurational assignment of *IE* and *IZ* from NMR data has been accomplished by Schmid and Heinola,² and the NMR shift data and positive entropy change in the direction taken to represent the *E*→*Z* isomerization (see Discussion) lead us to the same conclusion.

Table 2. Thermodynamic data at 298.15 K for the *E*→*Z* isomerization reactions studied in this work. Solvent: cyclohexane. The errors are twice the standard errors.

Com- pound	Eqn. ^a	$\Delta G^\ominus /$ kJ mol ⁻¹	$\Delta H^\ominus /$ kJ mol ⁻¹	$\Delta S^\ominus /$ J K ⁻¹ mol ⁻¹	$\Delta C_p^\ominus /$ J K ⁻¹ mol ⁻¹
I	C	-1.60(6)	1.8(8)	11.5(25)	-22(14)
V	C	-1.08(3)	2.6(5)	12.5(17)	-18(11)
VI	L	-1.52(5)	0.1(3)	5.5(9)	...
VII	C	2.24(4)	5.3(5)	10.1(17)	-25(9)
VIII	C	1.07(4)	3.8(7)	9.2(23)	-20(14)
IX	L	2.94(10)	5.4(6)	8.1(18)	...
X	C	-1.70(5)	1.2(8)	9.6(25)	-12(15)
XI	L	-0.08(1)	2.2(1)	7.7(3)	...
XII	L	-5.73(7)	-12.3(5)	-22.0(16)	...

^a The equation used in the calculations: L=van't Hoff eqn. (linear), C=eqn. (3) (curvilinear).

RESULTS

In most cases $\ln K$ proved to be a nonlinear function of T^{-1} (i.e. $\Delta C_p^\ominus \neq 0$). Then the experimental values of K were fitted to the equation³

$$\ln K = A + BT^{-1} + C \ln T \quad (3)$$

from which the values of ΔC_p^\ominus (independent of T) could be obtained. The values of the thermodynamic parameters, derived from the van't Hoff equation ($\Delta C_p^\ominus = 0$) or eqn. (3), are shown in Table 2. In the synthetic products of the *para*-substituted compounds, II–VI, the *E*:*Z* ratio was about 0.5 suggesting that for all these compounds the values of the thermodynamic parameters of the *E*→*Z* isomerization are similar. Hence only one of them (V) was equilibrated.

DISCUSSION

It is likely that conjugation between the olefinic double bond and the (substituted) phenyl group (compounds I–IX and XII) is more enhanced in the *Z* isomer, since there are fewer resonance-inhibiting steric interactions between the aromatic ring and the rest of the molecule in this configuration (cf. styrene appears⁴ to be a planar molecule, but the interplanar angle between the planes of the aromatic ring and the double bond in *cis*- β -methylstyrene is^{4,5} about 30–35°). Thus it might be expected that the inductive and resonance effects of the substituents could

affect the extent of conjugation in the two isomers in unequal amounts. However, the data shown in Table 2 reveal that only *ortho*-substituents can significantly alter the relative stability of the *E,Z* pair. Hence the relative stability is mainly affected by the steric effect of the particular substituent, and this effect is negligible for substituents in the *meta*- or *para*-position. *ortho*-Substituents raise the relative enthalpy of the *Z* isomer suggesting that the decrease in conjugation caused by *ortho*-substitution is more severe in the *Z* isomer. The steric requirements of *ortho*-substituents are also reflected in the standard enthalpies of formation of some isomeric derivatives of benzoic acid: the *o*-Me, *o*-F, *o*-Cl, and *o*-I derivatives have less negative $\Delta H_f^\ominus(c)$ -values than the corresponding *m*- and *p*-derivatives.⁶ Similarly, steric effects affect the carbonyl frequency, νCO , in *ortho*-substituted acetophenones, benzoic acids, etc.^{7,8}

2-Furyl and 2-thienyl groups are practically equivalent to a phenyl group as to their effect on the enthalpy and entropy difference between the geometric isomers.

The NMR shift data (Table 1) are interesting. In the *E* form of compounds I–XI, the signal of the MeO group is constantly found at $\delta 3.53 \pm 0.03$ and that of the olefinic proton at about $\delta 4.7$ (max. 4.74, min. 4.59). The inability of R to affect the position of the signal of the MeO group is understandable if this group exists in the planar *s-cis* configuration (the most stable configuration of methyl vinyl ether, see Ref. 9 and the references cited therein), in which the distance R··Me (in MeO) has the maximum value. Similarly, the signal of the β methyl group of the *Z* isomer is found at $\delta 1.72 \pm 0.02$. However, *ortho*-substituents move (i) the signal of the β methyl group in the *E* isomer about 0.25 ppm to a higher field, and (ii) the signals of the MeO group and the olefinic proton in the *Z* isomer 0.1–0.2 and 0.3–0.6 ppm, respectively, to a higher field. This is reasonable, since *ortho*-substituents inevitably increase the interplanar angle between the aromatic ring and the double bond in both isomers. Thus the "face" of the phenyl group is forced to turn towards the β *cis* substituent (Me or H), and the *shielding* diamagnetic anisotropy effect¹⁰ of the aromatic ring (for protons above or below the plane of the ring) leads to the upfield shifts

observed. In the *Z* isomer, the MeO group probably assumes the *gauche* or *s-trans* configuration (see previous papers of this series), and the shielding effect of the aromatic ring is also directed towards this group. It is remarkable that in the *E* isomers of X and XI the signal of the β methyl group is found at about $\delta 1.85$, i.e. 0.2 ppm to a lower field than the corresponding signal in I–IX. This might imply that the interplanar angle in *XE* and *XIE* is very small whereby the *deshielding* diamagnetic anisotropy effect of the furan and thiophene rings¹⁰ causes the downfield shifts observed. If this interpretation is correct, the coplanarity must be ascribed to the smaller steric requirements of the five-membered rings in question.

For R=Me in reaction (1), $\Delta H_1^\ominus = 10.3 \pm 0.3$ kJ mol⁻¹ and $\Delta S_1^\ominus = 13.9 \pm 0.8$ J K⁻¹ mol⁻¹.¹¹ Since the entropy change is positive, it might be assumed that this should be the case for *IE*→*IZ*, too, and our configurational assignment for these isomers, based on the NMR shift data, is in agreement with this expectation. The difference (about 8 kJ mol⁻¹) between the values of ΔH_1^\ominus for the two reactions in question exceeds the difference (about 3 kJ mol⁻¹, Ref. 12) between Me··Me and Me··Ph *cis* interaction energies, which affect the stability of the *E* isomers. Thus it appears that *IZ* has some unexpected stabilization.

Replacement of the MeO group in I by an Et₂CHO group (XII) favors the stability of the *Z* isomer, in agreement with some previous results.¹³ On going from I to XII, the increments in the values of the thermodynamic functions of isomerization are the following: $\Delta(\Delta G_1^\ominus) = -4.1$ kJ mol⁻¹, $\Delta(\Delta H_1^\ominus) = -14.1$ kJ mol⁻¹, and $\Delta(\Delta S_1^\ominus) = -34$ J K⁻¹ mol⁻¹. For R=Me in reaction (1) the corresponding increments are¹³ as follows: $\Delta(\Delta G_1^\ominus) = -4.3$ kJ mol⁻¹, $\Delta(\Delta H_1^\ominus) = -8.3$ kJ mol⁻¹, and $\Delta(\Delta S_1^\ominus) = -13$ J K⁻¹ mol⁻¹.

Acknowledgement. The authors are indebted to Mr. Pentti Ylivainio for some experimental aid.

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Received June 4, 1975.