

Thermodynamics of Vinyl Ethers. X.* The Stabilizing Effect of β -Phenyl Substitution on α,β -Unsaturated Ethers

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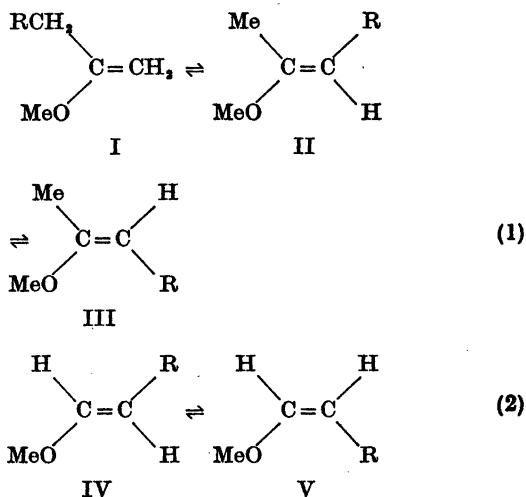
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The effect of β -phenyl substitution on the thermodynamic stability of α,β -unsaturated (olefinic) ethers has been studied by means of chemical equilibration of suitable isomeric compounds. The stabilizing energy of a β -phenyl substituent was obtained as 15 ± 2 kJ mol⁻¹. The destabilizing methyl-phenyl *cis* interaction energy across a double bond was evaluated as 7.5 ± 1.5 kJ mol⁻¹.

Almost forty years ago Kistiakowsky and co-workers¹ started their investigations of the enthalpies of hydrogenation of unsaturated compounds, including a number of variously substituted ethenes. The large amount of thermochemical data obtained shed much light on the factors affecting the stability of olefinic compounds. It was found, for instance, that if one or several of the hydrogen atoms of ethene were replaced by alkyl groups² or unsaturated groups, such as vinyl or phenyl groups,³ considerably less heat was liberated in the hydrogenation of the ethylenic bond than was produced in the hydrogenation of ethene itself. This was regarded as indicative of the enhanced stability of the ethylenic system due to the particular substituent involved. The enthalpy of hydrogenation of the ethylenic linkage of styrene (phenylethene) was about 18 kJ mol⁻¹ more positive than that of ethene in the gas phase at 355 K,^{1,3} which shows that in olefins a phenyl group linked to the double bond causes a stabilization of about 18 kJ mol⁻¹.

The previous studies of this series have revealed that the double bond of a vinyl ether

is not as effectively stabilized by alkyl groups as that of an "ordinary" olefin. Hence it was of interest to find out whether the same phenomenon could be observed if the double bond of a vinyl ether were substituted by a phenyl group. For that purpose, thermodynamics of interconversion of the vinyl ethers I–V were investigated (R = Ph).



On going from I to II (or from I to III), a phenyl group is transferred from a nonconjugated allylic position to a site where conjugation with the vinyl group is possible. The value of $\Delta H^\circ(\text{g})$ for this reaction (I→II), corrected by the value of the destabilizing Me–Ph *cis* interaction energy, is taken to represent the stabilizing energy of β -phenyl substitution in vinyl ethers. The value of the Me–Ph *cis* interaction energy was determined by compar-

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ing the changes in standard enthalpy for reactions II→III and IV→V in cases R=Ph and R=Me. Thermodynamic data for the case R=Me have been published previously in this series.

EXPERIMENTAL

Syntheses. I, II and III. A 45 % yield of a mixture of I, II and III (11 % I, 74 % II and 15 % III) was obtained when a mixture of benzyl methyl ketone (0.20 mol), trimethyl orthoformate (0.25 mol) and methanol (50 cm³) was slowly distilled in the presence of a small amount of *p*-toluenesulfonic acid,⁴ first at atmospheric, finally at reduced pressure. The mixture was collected at 359 to 365 K at 1.0 kPa. **IV and V.** A 65 % yield of a mixture of IV and V (64 % IV, 36 % V) could be collected at 481 to 483 K at 99.1 kPa when 0.17 mol of the dimethyl acetal of 2-phenylacetaldehyde (obtained from Aldrich) were fractionated from a catalytic amount of *p*-toluenesulfonic acid. **NMR spectra.** The NMR spectra were recorded on a 60 MHz Perkin Elmer R 10 spectrometer at 307 K. Carbon tetrachloride was used as solvent and TMS as internal standard. *I*: τ 6.69 ($-\text{CH}_2-$) 6.56 ($-\text{CH}_3$), 6.19 (H *trans* to MeO),

6.12 (H *cis* to MeO), 2.8 (aromatic protons), $J(=\text{CH}_2)$ 1.7 Hz; *II*: τ 8.07 ($\text{CH}_3-\text{C}=\text{C}$), 6.46 ($\text{CH}_3-\text{O}-$), 4.50 (H-C=), 2.9 (aromatic protons); *III*: τ 8.07 ($\text{CH}_3-\text{C}=\text{C}$), 6.41 ($\text{CH}_3-\text{O}-$), 4.77 (H-C=), 2.9 (aromatic protons); *IV*: τ 6.43 ($\text{CH}_3-\text{O}-$), 4.23 (H *cis* to MeO), 2.97 (H-C \leq O), 2.9 (aromatic protons), J_{vic} 13.5 Hz; *V*: τ 6.34 ($\text{CH}_3-\text{O}-$), 4.82 (H *trans* to MeO), 3.97 (H-C \leq O), 2.9 (aromatic protons), J_{vic} 7.2 Hz.

Determination of normal boiling temperatures. The normal boiling temperatures of the compounds studied were determined by the gas-chromatographic method described earlier.⁵ *I, II and III*: reference curve (compound, boiling temperature at 101.3 kPa, relative retention time): 1-methoxycyclohexene, 417.1 K, 0.238; 1-ethoxycyclohexene, 435.0 K, 0.327; 1-propoxycyclohexene, 455.9 K, 0.518; 1-cyclopentoxycyclopentene, 479.7 K, 1.000. The relative retention times of I, II and III were 0.735, 1.036 and 1.304 corresponding to normal boiling temperatures of about 469.7, 480.2 and 485.2 K, respectively. *IV and V*: the retention times of IV and V were equal implying that the boiling temperatures of the two isomers are also equal. Therefore, the thermodynamic functions of isomerization of IV to V are equal in the vapor and liquid phases,⁵ and hence the boiling temperatures need not be known.

Table 1. Values of the mean equilibrium constant *K* and its standard error for the isomerization reactions involving the compounds: 2-methoxy-3-phenylpropene (I), (*E*)-2-methoxy-1-phenylpropene (II), (*Z*)-2-methoxy-1-phenylpropene (III), (*E*)-1-methoxy-2-phenylethene (IV), and (*Z*)-1-methoxy-2-phenylethene (V). The number of independent determinations is denoted by *n* and the letters A, B, C, and D refer to the various initial mixtures used (see text). Solvent: cyclohexane.

Temp. °K	Initial mixture	<i>n</i>	K_1 (II/I)	K_2 (III/I)	K_3 (III/II)	K_4 (V/IV)
295.2	A	2	14.8 ± 0.4	2.25 ± 0.05	0.153 ± 0.002	
311.2	A	2	11.6 ± 0.1	2.13 ± 0.04	0.185 ± 0.004	
326.2	A	2	10.2 ± 0.2	2.10 ± 0.05	0.207 ± 0.002	
336.2	A	3	9.40 ± 0.10	2.09 ± 0.05	0.223 ± 0.001	
354.2	A	9	7.31 ± 0.07	1.74 ± 0.03	0.238 ± 0.005	
355.2	B	2	7.55 ± 0.08	1.92 ± 0.04	0.253 ± 0.001	
373.2	A	9	6.83 ± 0.09	1.80 ± 0.03	0.268 ± 0.006	
388.2	A	4	6.09 ± 0.16	1.84 ± 0.05	0.302 ± 0.001	
395.2	C	3	5.54 ± 0.06	1.74 ± 0.03	0.317 ± 0.009	
404.2	A	3	5.25 ± 0.06	1.68 ± 0.07	0.322 ± 0.042	
423.2	A	2	4.82 ± 0.01	1.65 ± 0.02	0.343 ± 0.004	
423.2	B	2	4.73 ± 0.01	1.68 ± 0.02	0.355 ± 0.005	
295.2	D	2				0.485 ± 0.001
326.2	D	4				0.498 ± 0.007
354.2	D	6				0.528 ± 0.007
375.2	D	2				0.533 ± 0.006
396.2	D	2				0.544 ± 0.001
407.2	D	4				0.551 ± 0.004

^a Accurate to ± 0.5 K.

Equilibration experiments. Prior to the equilibrations, the substrates were purified by preparative GLC (the column contained 10% SE-30 on Chromosorb G), if possible. However, IV and V could not be separated owing to the similar retention times. Three different fractions of I, II and III were thus available for the equilibrations: (A): 11% I, 74% II and 15% III; (B): 100% II; (C): 75% I, 21% II and 3% III. The equilibrations of I, II and III were conducted in cyclohexane with iodine as catalyst. The total substrate concentration was 1.2 mol dm⁻³ and the catalyst concentration 0.006 mol dm⁻³. The equilibrated samples were analyzed by GLC by means of a 4 m column containing 10% SE-30 on Chromosorb G. Peak separation was good. The relative retention times of I, II and III were 0.57, 0.78 and 1.000, respectively. Column temperature was kept at 388 K. Under these conditions, partial isomerization of the samples injected was found to occur unless sufficient amounts (about 5 μl) of diethylamine were injected into the column immediately before injection of the equilibrated sample.

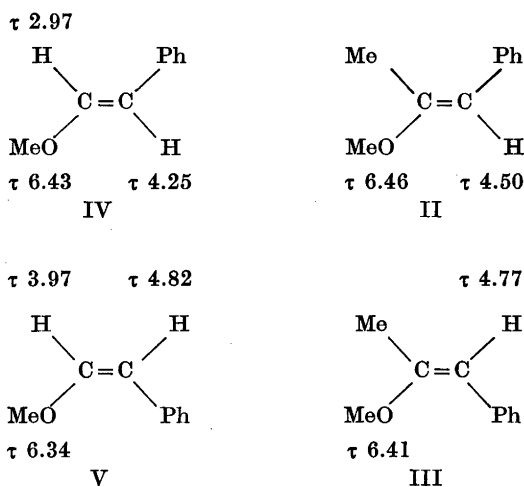
The equilibration of IV and V was conducted in the neat liquid with mercuric acetate as catalyst. Catalyst concentration was 0.24 mol dm⁻³. The synthetic product (denoted by D in Table 1) containing 64% of IV and 36% of V was used as the initial mixture for the equilibrations. The peaks of IV and V were satisfactorily separated in the analytical column used (an 8 m column containing 10% Carbowax 20 M on Chromosorb G), when long retention times (148 min for IV, 154 min for V) were used. These compounds are much less reactive than I, II and III, and hence no isomerization was found to take place during the analyses (column temperature 423 K). However, prior to analysis the equilibrated samples were diluted with an equal volume of diethylamine to maintain alkaline conditions in the column. Equilibrium was considered having been reached when the isomer ratio remained constant in successive samples taken over sufficiently extended periods of time. The relative peak areas were determined by the cut-and-weigh method.

Additional details of the practical performance of the equilibrations are found in the previous papers of this series.

CONFIGURATIONAL ASSIGNMENT OF THE GEOMETRIC ISOMERS

The *Z* and *E* forms⁶ of 1-methoxy-2-phenylethene (V and IV, respectively) are easily identified, since the value of the vicinal coupling constant between the olefinic protons in the *Z* form of a disubstituted ethene is known to be about a half of that in the *E* form.⁷ In the present case, the coupling constants were 7.2

and 13.5 Hz; hence the compound possessing the larger coupling constant was taken as the *E* isomer (IV). On the other hand, configurational assignment of the geometric isomers of 2-methoxy-1-phenylpropene (II and III) is more complicated. Kresge and Chen⁸ have prepared the same pair of isomers and they observed that one of the isomers gave a methyl group NMR signal at τ 8.07 and the other at τ 8.27. From this they concluded that the former or the more volatile isomer should be β -methoxy-*trans*- β -methylstyrene, *i.e.* (*Z*)-2-methoxy-1-phenylpropene (III). In support of this assignment they gave some synthetic evidence. Kresge and Chen did not specify the possible solvent used in the NMR experiment but we have not been able to detect any difference in the positions of the methyl signals derived from the two isomers when the spectra were taken in CCl₄ solution. Moreover, it appears that in compounds of the type studied in this work, the isomer having methyl *trans* to phenyl does not always give a methyl group NMR signal at a lower field than the other geometric isomer, contrary to the assumption of Kresge and Chen. Thus Rummens and de Haan⁹ have published NMR data for the geometric isomers of 1-phenylpropene: in the neat liquid the isomer having Me *trans* to Ph gave a methyl group signal about 0.03 ppm *upfield* from that of the *cis* form. On the basis of the following reasoning it appears that the configurational assignment of the geometric isomers of 2-methoxy-1-phen-



Scheme 1.

ylpropene, proposed by the above authors, is erroneous.

First, the NMR data reveal some interesting features. In the presentation in Scheme 1, the structures of the geometric isomers of 2-methoxy-1-phenylpropene have been drawn with the assumption that the more volatile isomer has the *E* configuration (II). On going from IV to V, the signal due to the β -proton (the proton bound to the same carbon as Ph) undergoes a shift of about 0.6 ppm to a higher field. A somewhat smaller shift in the same direction is expected on going from II to III, since replacement of a hydrogen atom in ethene or a substituted ethene by a methyl group causes a larger upfield shift in the position of the signal due to the proton *trans* to the group introduced. If the *E* and *Z* forms of 2-methoxy-1-phenylpropene are taken as proposed above, the shift in question is about 0.3 ppm to a higher field, in agreement with expectation. If the configurational assignment suggested by Kresge and Chen were correct, the signal of the β -proton would be removed about 0.3 ppm *downfield* on going from the *E* form to the *Z* form, which is hardly acceptable in view of the about 0.6 ppm *upfield* shift in the case IV \rightarrow V.

Considering the two *Z* forms V and III, the signal of the β -proton is found at about τ 4.8 in each case. This is reasonable, since replacement of the α proton in V by a methyl group has no effect on the spatial orientation of the phenyl group in a *trans* position relative to the proton replaced. Moreover, in each *E*–*Z* isomer pair studied, the signal of the methoxy group of the *E* form is found at a somewhat higher field than that of the *Z* form, although the difference in the positions of the signals is very small.

Further evidence for the configurational assignment proposed above is obtained from the equilibration data. It has been shown that of the geometric isomers of an α,β -dialkylsubstituted vinyl methyl ether the one having the higher entropy value is the *Z* form.^{4,5} In the present case, the entropy of the less volatile isomer is about 7.3 J K⁻¹ mol⁻¹ higher than that of the other geometric isomer, and hence we are apt to regard the former as the *Z* form.

RESULTS

The primary results of the equilibration experiments are shown in Table 1. From the values of the mean equilibrium constant at various temperatures, the values of ΔG° , ΔH° and ΔS° at 298.15 K for each isomerization reaction involved were calculated as described previously.¹⁰ The results are collected in Table 2. Finally, the values of ΔH° and ΔS° in the ideal gas state at 298.15 K were evaluated from the liquid phase data and the normal boiling temperatures (Table 3).⁵

DISCUSSION

Let us consider the changes in standard enthalpy and standard entropy accompanying reaction (3), for which experimental data are given in Table 4. In the case R²=Me, the

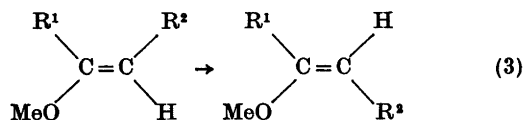


Table 2. Values of the thermodynamic functions ΔG° , ΔH° and ΔS° for isomerization reactions involving the compounds given in Table 1. The solvent is cyclohexane and the temperature 298.15 K. The errors are twice the standard errors.

Reaction	$\Delta G^\circ/\text{kJ mol}^{-1}$	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
I \rightarrow II	-6.51 ± 0.10	-9.0 ± 0.5	-8.4 ± 1.2
I \rightarrow III	-2.00 ± 0.12	-2.5 ± 0.6	-1.8 ± 1.4
II \rightarrow III	4.50 ± 0.08	6.5 ± 0.4	6.6 ± 1.0
IV \rightarrow V	1.80 ± 0.04	1.2 ± 0.2	-2.1 ± 0.5

Table 3. Values of the thermodynamic functions ΔH° and ΔS° in the gas phase at 298.15 K for the isomerization reactions involving the compounds mentioned in Table 1.

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
I \rightarrow II	-7.3 ± 0.6	-6.8 ± 1.3
I \rightarrow III	0.0 ± 0.6	0.5 ± 1.5
II \rightarrow III	7.3 ± 0.5	7.3 ± 1.1
IV \rightarrow V	1.2 ± 0.4	-2.1 ± 0.7

Table 4. Experimental data for reaction (3).

R ¹	R ²		$\Delta H^\circ(g)/\text{kJ mol}^{-1}$	$\Delta S^\circ(g)/\text{J K}^{-1} \text{mol}^{-1}$	Remarks
H	Me		0.43	2.9	Ref. 11
Me	Me		9.85	13.4	Ref. 4
		Increase	9.4	10.5	
H	Ph		1.2	-2.1	This work
Me	Ph		7.3	7.3	This work
		Increase	6.1	9.4	

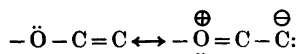
increase in $\Delta H^\circ(g)$ on going from R¹=H to R¹=Me is about 9.4 kJ mol⁻¹, while the increase is only about 6.1 kJ mol⁻¹ in the case R²=Ph. This shows that the Me-Ph *cis* interaction is about 9.4 - 6.1 = 3.3 kJ mol⁻¹ higher than the Me-Me interaction, which is obtained as 4.2 kJ mol⁻¹ from the difference in the standard enthalpies of (*Z*)-2-butene and (*E*)-2-butene.¹² Hence the Me-Ph *cis* interaction energy may be evaluated as 3.3 + 4.2 = 7.5 kJ mol⁻¹ with an estimated accuracy of ± 1.5 kJ mol⁻¹. This result is in slight disagreement with a reported enthalpy difference (about 4.2 kJ mol⁻¹) between the geometric isomers of 1-phenylpropene.¹³ On the other hand, theoretical calculations¹⁴ suggest a value of about 11 kJ mol⁻¹ for the same enthalpy difference. It is of interest that the same calculations¹⁴ of the relative enthalpies of the geometric isomers of 2-phenyl-2-butene show that the isomer with methyl *cis* to phenyl should have an enthalpy about 3.3 kJ mol⁻¹ higher than that of the other isomer with the two methyl groups in a *cis* position. Since the difference 3.3 kJ mol⁻¹ can be regarded as arising from the difference between Me-Ph and Me-Me *cis* interaction energies, the value of the former is obtained as 3.3 + 4.2 = 7.5 kJ mol⁻¹, which is exactly equal to that achieved in this study.

The value of the Me-Ph *cis* interaction energy, 7.5 ± 1.5 kJ mol⁻¹, is reasonable in the light of the values of the Me-Me and Ph-Ph *cis* interaction energies. The former is known to be about 4.2 kJ mol⁻¹,¹² while the values reported for the Ph-Ph *cis* interaction energy are somewhat scattered. Thus Kistiakowsky and Smith¹⁵ obtained the enthalpy difference between gaseous (*Z*)- and (*E*)-stilbene as about 12 kJ mol⁻¹, and Fischer *et al.*¹⁶ reported the enthalpy of the *Z* form to be 12.1 ± 1.2 kJ mol⁻¹

higher than that of the *E* form in methylcyclohexane. From the "selected values" of Cox and Pilcher,¹⁷ the value of $\Delta H^\circ(g)$ in (*E*)-stilbene \rightarrow (*Z*)-stilbene is obtained as about 16 kJ mol⁻¹, if the standard enthalpy of formation of crystalline (*E*)-stilbene is combined with the enthalpy of vaporization data reported by Morawetz.¹⁸ Hence the most probable value of the Ph-Ph *cis* interaction energy seems to be 12 to 16 kJ mol⁻¹, *i.e.* about twice the value of the Me-Ph *cis* interaction energy.

The stabilizing effect of β -phenyl substitution (excluding destabilizing *cis* interactions) is now obtained as about 15 kJ mol⁻¹, with an estimated error of ± 2 kJ mol⁻¹, since the observed enthalpy change for I \rightarrow II, -7.3 kJ mol⁻¹, is a composite of the true stabilizing effect of the β -phenyl substituent and the destabilizing *cis* interaction energy, 7.5 kJ mol⁻¹. This figure (15 kJ mol⁻¹) may be compared with the stabilizing effect of β -phenyl substitution on an "ordinary" olefinic double bond. As mentioned previously, a phenyl group stabilizes the double bond of ethene by about 18 kJ mol⁻¹ (as determined from enthalpies of hydrogenation), while the group parameters of Benson *et al.*¹⁹ suggest an enthalpy change of about -21 kJ mol⁻¹ for the reaction 3-phenylpropene \rightarrow 1-phenylpropene (neglecting steric corrections), which corresponds to the reaction I \rightarrow II (R = Ph) with the methoxy groups replaced by hydrogen atoms. Hence in vinyl ethers, a β -phenyl substituent causes a stabilization 3 to 6 kJ mol⁻¹ lower than that brought about by the same substituent on ordinary olefins. Qualitatively, this result compares well with the weak stabilizing power of alkyl groups on the double bond of vinyl ethers: the enthalpy change, 0.45 kJ mol⁻¹,⁴ for 2-methoxy-1-butene \rightarrow (*E*)-2-methoxy-2-butene is about 9 kJ mol⁻¹ more positive

than that (-8.4 kJ mol^{-1} , Ref. 12) for the reaction between the corresponding olefins, 1-butene \rightarrow (*Z*)-2-butene. These facts are explainable in terms of the reduced double-bond character of the ethylenic system of vinyl ethers, which is a result of electron delocalization involving the lone-pair electrons of the oxygen atom and the π -electrons of the double bond:



The entropy change ΔS° (g) in the reaction I \rightarrow II (R = Ph) is $-6.8 \text{ J K}^{-1} \text{ mol}^{-1}$. The group parameters of Benson *et al.*¹⁹ predict an entropy change of about $-13.8 \text{ J K}^{-1} \text{ mol}^{-1}$ for the reaction between the corresponding hydrocarbons, 3-phenylpropene \rightarrow (*Z*)-1-phenylpropene (neglecting *cis*-correction). According to the API values,¹³ the entropy of (*Z*)-1-phenylpropene is about $3.4 \text{ J K}^{-1} \text{ mol}^{-1}$ higher than that of the *E* isomer. Taking this figure to represent the value of the *cis*-correction term in (*Z*)-1-phenylpropene, the calculated entropy change for 3-phenylpropene \rightarrow (*Z*)-1-phenylpropene is obtained as $-13.8 + 3.4 = -10.4 \text{ J K}^{-1} \text{ mol}^{-1}$, which is about $4 \text{ J K}^{-1} \text{ mol}^{-1}$ more negative than the value of ΔS° (g) in I \rightarrow II. The reason for this difference is not clear.

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