

## Thermodynamics of Vinyl Ethers. XXVIII.\* Effects of Steric Strain on the Stability of a C=C–Ph System

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The effects of increasing steric crowding on the thermodynamics of certain isomerization reactions have been studied. The reactions concerned include the isomerizations of variously substituted 2-methoxy-3-phenylpropenes to the corresponding 2-methoxy-1-propenes as well as the isomerizations of some 2-methoxy-1,4-dihydronaphthalenes to the respective 3,4-dihydro derivatives. The thermodynamic stabilities of the conjugated isomers with a C<sub>2</sub>=C<sub>1</sub>–Ph moiety are markedly decreased by substituents either at the C<sub>1</sub> position or at an *ortho* position of the aromatic ring.

We have previously<sup>1</sup> published an investigation concerning the double-bond stabilization ability of a Ph group in alkyl vinyl ethers. From an equilibrium study of reaction 1 with X=R=H it was inferred that, excluding the effects of steric interactions between the Ph group and the neighboring atoms (mainly those of the *cis* Me group) in *1b*, the Ph group stabilizes the C=C bond by 15±2 kJ mol<sup>-1</sup>, *i.e.* slightly less than in corresponding phenyl-substituted olefins. We have now studied the thermodynamics of reaction 1 using sterically more crowded compounds (2–4). For comparison, we have also investigated the thermodynamics of reaction 2 in which the key feature is similarly the transfer of a C=C bond from an allylic to a vinylic position, relative to the aromatic ring.

### RESULTS AND DISCUSSION

The results of the equilibration experiments are summarized in Tables 1 and 2, together with some literature data. As expected, a meta substituent has only a minor effect on the thermodynamics of reaction 1 (Table 2). Maybe the most noteworthy effect is observed in the *a*→*c* reaction for which the value of  $\Delta H^\ominus(1)$  is *ca.* 2 kJ mol<sup>-1</sup> less negative for X=*m*-Me than for X=H, suggesting a slight destabilizing steric interaction between the substituent and neighboring atoms in *2c*. On the other hand, an *ortho* substituent has a marked effect on the relative isomer stabilities, the  $\Delta H^\ominus$  values of both the *3a*→*3b* and *3a*→*3c* reactions being *ca.* 5 kJ mol<sup>-1</sup> more positive than those for the corresponding reactions involving the unsubstituted compounds. Clearly, the *o*-MeO substituent prevents the *b* and *c* isomers from adopting an efficient conformation with the unsaturated system coplanar with the benzene

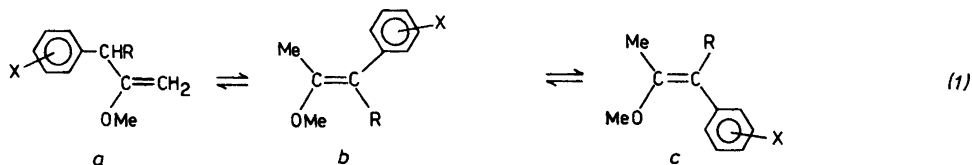
\* Part XXVII. Taskinen, E. and Mukkala, V.-M. *Tetrahedron* 38 (1982) 613.

Table 1. Compositions of the equilibrium mixtures at various temperatures.

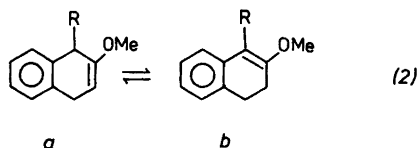
Compound No.	T/K	$c_a$ /%	$c_b$ /%	$c_c$ /%
2	314	7.87	81.89	10.24
	355	10.27	76.39	13.35
	379	11.59	72.89	15.53
	398	12.95	70.47	16.58
	421	14.12	67.80	18.08
3	271	13.18	81.94	4.87
	297	15.90	78.40	5.69
	323	16.53	76.90	6.57
	373	19.63	71.88	8.48
	403	19.43	71.12	9.44
4	271	38.17	8.02	53.82
	297	35.55	8.28	56.17
	323	32.83	10.70	56.47
	373	29.71	15.63	54.66
	403	29.09	16.81	54.10
5	373		100.0	
6	298	6.29	93.71	
	333	6.94	98.06	
	363	7.14	92.86	
	373	7.41	92.59	
	393	7.41	92.59	
	423	8.33	91.67	

ring. The corresponding reaction entropies are also seen to be increased by the ortho substituent.

An essential change in the thermodynamics of reaction 1 occurs when one of the allylic H atoms of the *1a* compound is replaced with a bulkier (Me) substituent: for the  $a \rightarrow b$  reaction the reaction enthalpy and entropy increase by 17 kJ mol<sup>-1</sup> and 24 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. This, of course, is due to the steric bulkiness of the Me group, which in the *b* isomer forces the MeO group to assume a high energy gauche conformation around the O-C(*sp*<sup>2</sup>) bond, instead of the planar low energy *s-cis* conformation for R=H.<sup>2</sup> For the sake of comparison, in reaction 3 the corresponding structural change (R=H to R=Me) increases the  $\Delta H^\circ(l)$  and  $\Delta S^\circ(l)$  values by 8 kJ mol<sup>-1</sup> and 19 J K<sup>-1</sup> mol<sup>-1</sup>, respectively.<sup>2,3</sup> The significantly higher effect on reaction enthalpy of the methyl substitution in the former case suggests that in *4b* the Me substituent has a strong conjugation decreasing effect, twisting the Ph group out of coplanarity with the olefinic system. In this compound the steric crowding around the aromatic ring is particularly tangible, due to simultaneous interactions with both a *cis* methyl and a *gem* methyl group.<sup>4</sup>



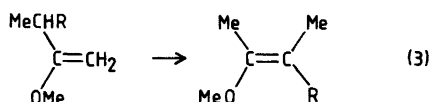
Scheme 1. 1; X=R=H; 2, X=*m*-Me, R=H; 3, X=*o*-MeO, R=H; 4, X=H, R=Me.



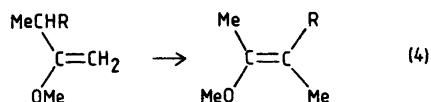
Scheme 2. 5, R=H; 6, R=Me.

The configurations of the geometrical isomers *4b* and *4c* were assigned on the basis of thermodynamic data of isomerization as follows. It has been previously shown that for R=H and R=Me in reaction 4 the values of  $\Delta H^\ominus$  are 8.5 and 6.5 kJ mol<sup>-1</sup> (cyclohexane solution, 298 K), respectively.<sup>2,3</sup> In this case the methyl substitution is seen to decrease the reaction enthalpy by 2 kJ mol<sup>-1</sup>. Similarly, one might expect that in the *a*→*c* isomerization (reaction 1) the effect of methyl substitution on  $\Delta H^\ominus$  should be of about the same magnitude. For R=H the reaction enthalpy for the *a*→*c* reaction is  $-2.5 \pm 0.6$  kJ mol<sup>-1</sup> while for R=Me one has to select between two alternative  $\Delta H^\ominus$  values:  $\Delta H_1^\ominus = 1.8 \pm 0.5$  kJ mol<sup>-1</sup> and  $\Delta H_2^\ominus = 7.8 \pm 1.5$  kJ mol<sup>-1</sup>. Now the methyl substitution is seen to increase the reaction enthalpy, either by 4 or by 10 kJ mol<sup>-1</sup>, depending on which of the two alternative  $\Delta H^\ominus$  values is taken to represent the *a*→*c* reaction enthalpy. In view of the magnitude of the effect of methyl substitution on the  $\Delta H^\ominus$  values of reaction 1 ( $-2$  kJ mol<sup>-1</sup>), the smaller of these values (4 kJ mol<sup>-1</sup>) seems to be the better choice and hence the  $\Delta H^\ominus$  value of  $1.5 \pm 0.5$  kJ mol<sup>-1</sup> is taken to belong to the *4a*→*4c* reaction. The more positive effect of methyl substitution on the  $\Delta H^\ominus$  value of reaction 1 is understandable since owing to the bulkiness of the Ph group (relative to a Me group) the steric strain is likely to be higher in *4c* than in the product of reaction 4.

In the equilibrium mixture *5a*⇌*5b* the conjugated form (*5b*) dominated to such an extent that the presence of the nonconjugated isomer could not be detected at 373 K. Hence it was concluded that the value of the equilibrium constant  $K(5b/5a)$  must be 100 or more which leads to  $\Delta G^\ominus \leq -14$  kJ mol<sup>-1</sup> for the *5a*→*5b* reaction at 373 K. For comparison, from enthalpies of hydrogenation in acetic acid at 302 K the value of  $\Delta H^\ominus$  for the isomerization of 1,4-dihydronaphthalene to 1,2-dihydronaphthalene is calculated to be *ca.*  $-13$  kJ mol<sup>-1</sup>.<sup>5</sup> In agreement with expectation, a Me substituent at C-4 of the 3-methoxy derivatives of these hydrocarbons decreases markedly the thermodynamic stability of the conjugated isomer, leading to a modest  $\Delta H^\ominus$  value of only  $-2.3$  kJ mol<sup>-1</sup> for the *6a*→*6b* reaction.



Scheme 3.



Scheme 4.

## EXPERIMENTAL

**Materials.** A mixture of *2a*, *2b* and *2c* was obtained by means of a Grignard reaction between 3-methylbenzylmagnesium chloride and 1,2-dibromoethyl methyl ether, followed by dehydrobromination with solid *t*-BuOK (for an analogous preparation see Ref. 6). From 40 g of 3-methylbenzyl chloride, a 23 % yield (10.6 g) of *2a* (19 %), *2b* (70 %) and *2c* (11 %) was obtained (boiling range 368–393 K at 1.3 kPa). By treatment of methyl 2-methoxybenzyl ketone with trimethyl orthoformate in methanol<sup>7</sup> one obtained a 84 % yield of a mixture of *3a* (20 %), *3b* (70 %) and *3c* (10 %), b.p. 394–396 K at 0.8 kPa. Similarly, a treatment of methyl 1-phenylethyl ketone with trimethyl orthoformate gave a 12 % yield of a mixture of *4a* (45 %), *4b* (8 %) and *4c* (47 %), b.p. 355–357 K at 0.8 kPa. The isomeric forms of *5* and *6* were also obtained by treatment of the appropriate ketones ( $\beta$ -tetralone for *5*,  $\alpha$ -methyl- $\beta$ -tetralone for *6*) with trimethyl orthoformate: *5b* (yield 93 %) b.p. 398 K at 1.3 kPa, *6a* (20 %)+*6b* (80 %) b.p. 402–423 K at 2.4 kPa, yield 91 %.

<sup>1</sup>H NMR spectra (60 MHz, CCl<sub>4</sub>,  $\delta$  values in ppm, *J* values in Hz). *2a*: 6.7–7.2 (aromatic protons), 3.8–3.9 (=CH<sub>2</sub>), 3.33 (–CH<sub>2</sub>–), 3.43 (MeO), 2.27 (Me). *2b*: 6.7–7.2 (aromatic protons), 5.44 (olefinic proton), 3.53 (MeO), 2.27 (Me), 1.92 (Me–C=C). *2c*: 6.7–7.2 (aromatic protons), 5.20 (olefinic proton), 3.57 (MeO), 2.27 (Me), 1.92 (Me–C=C). *3a*: 6.6–7.2 (aromatic protons), 3.76 (MeO), 3.83 (olefinic proton, the other olefinic proton signal was obscured by the MeO group signals), 3.47 (MeO–C=C), 3.33 (–CH<sub>2</sub>–). *3b*: 6.6–7.2 (aromatic protons), 5.51 (olefinic proton), 3.76 (MeO), 3.63 (MeO–C=C), 1.89 (Me). *3c*: 6.6–7.2 (aromatic protons), 5.63 (olefinic proton), 3.76 (MeO), 3.63 (MeO–C=C), 2.02 (Me). *4a*: 7.2 (aromatic protons), 4.05 and 4.32 (olefinic protons, *J* 2.4), 3.50 (MeO), 1.37 (Me, *J* 6.7), the signal of the methine proton was not detected. *4b*: 7.2 (aromatic protons), 3.46 (MeO), 1.90 (two Me groups). *4c*: 7.2 (aromatic protons), 3.56 (MeO), 1.76 (Me), 1.90 (Me). *5b*: 6.75 (aromatic protons), 5.32 (olefinic proton), 3.51 (MeO), 2.1–3.0 (–CH<sub>2</sub>CH<sub>2</sub>–). *6a*: 7.0 (aromatic protons), 4.60 (olefinic proton, *J* 4), 3.2–3.7 (CH<sub>2</sub>+CH), 3.52 (MeO), 1.33 (Me, *J* 6.6). *6b*: 6.9 (aromatic protons), 3.47 (MeO), 2.0–3.0 (–CH<sub>2</sub>CH<sub>2</sub>–), 1.91 (Me).

**Equilibrations.** The equilibration experiments were carried out in cyclohexane solution with I<sub>2</sub> as catalyst (for details, see refs. 1 and 2). The equilibrium mixtures were analyzed by GLC using the following packed columns: 4–8 m columns containing 10 % SE-30 on Chromosorb G for 2–4 (the compounds were eluted in the order *2a*, *2b*, *2c*; *3a*, *3b*, *3c*; *4a*, *4c*, *4b*), a 4 m column containing 10 % Carbowax 20 M on Chromosorb G for *5* and *6* (order

Table 2. Values of the thermodynamic parameters  $\Delta G^\ominus$ ,  $\Delta H^\ominus$  and  $\Delta S^\ominus$  for the various reactions investigated (298.15 K, cyclohexane solution). The errors are twice the standard errors.

Reaction	Compound no.	$\Delta G^\ominus/\text{kJ mol}^{-1}$	$\Delta H^\ominus/\text{kJ mol}^{-1}$	$\Delta S^\ominus/\text{J K}^{-1} \text{mol}^{-1}$
<i>a</i> → <i>b</i>	<i>1</i> <sup>a</sup>	–6.51(0.10)	–9.0(0.5)	–8.4(1.2)
	<i>2</i>	–6.24(0.08)	–8.0(0.3)	–6.0(0.9)
	<i>3</i>	–4.06(0.16)	–3.6(0.9)	1.6(2.7)
	<i>4</i>	3.32(0.26)	7.8(1.5)	15 (4)
	<i>5</i>	≤–14 <sup>b</sup>		
	<i>6</i>	–6.72(0.16)	–2.3(0.8)	14.7(2.0)
<i>a</i> → <i>c</i>	<i>1</i> <sup>a</sup>	–2.00(0.12)	–2.5(0.6)	–1.8(1.4)
	<i>2</i>	–0.69(0.13)	–0.2(0.6)	1.7(1.6)
	<i>3</i>	2.42(0.16)	2.1(0.9)	–1.1(2.6)
	<i>4</i>	–1.12(0.09)	1.8(0.5)	9.8(1.6)
<i>b</i> → <i>c</i>	<i>1</i> <sup>a</sup>	4.50(0.08)	6.5(0.4)	6.6(1.0)
	<i>2</i>	5.55(0.08)	7.8(0.4)	7.5(1.0)
	<i>3</i>	6.47(0.06)	5.7(0.3)	–2.7(1.0)
	<i>4</i>	–4.4 (0.03)	–6.0(1.7)	–5 (5)

<sup>a</sup> Ref. 1. <sup>b</sup> At 373 K.

of elution 6a, 6b). The compositions of the equilibrium mixtures at various temperatures are shown in Table 1 and the values of the thermodynamic parameters of reaction at 298.15 K in Table 2.

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