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Thermodynamics of Vinyl Ethers. XXIV.* Relative Stabilities and Structures of Some Isomeric Derivatives of Phenyl Vinyl Ether

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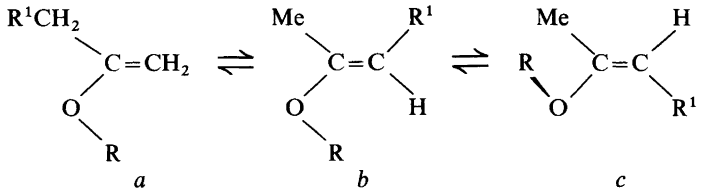
The relative stabilities of 2-aryloxy-4-methyl-1-pentenes (aryl = C_6H_5, 2-$CH_3-C_6H_4$ and 2,6-$(CH_3)_2-C_6H_3$) and the *E* and *Z* forms of the corresponding 2-pentenes have been determined by chemical equilibration in cyclohexane solution at several temperatures. The increasing steric requirements of the phenyl group following the introduction of *o*-substituents decrease the thermodynamic stability of the 2-pentenes relative to the 1-pentenes. This result is explained by means of stereochemical changes in the phenyl vinyl ether skeleton caused by the *o*-substituents. The probable conformations of the isomeric forms are discussed on the basis of thermodynamic, ^{13}C NMR and ^1H NMR data. A re-estimation of the relative enthalpies of the *gauche* and s-*cis* rotamers of methyl vinyl ether suggests that the enthalpy of the former is *ca.* 23 kJ mol^{-1} higher than that of the latter instead of the enthalpy difference of 12 kJ mol^{-1} proposed earlier.

In some previous papers[1-3] we have examined the effects of the size and nature of the alkoxy group of some isomeric alkoxy-substituted alkenes on their relative thermodynamic stabilities using chemical equilibration as the experimental method of investigation. One of the reactions studied is reaction (1). It was found that the relative stability of the *b* and, especially, of the *c* isomer is markedly increased by the increasing bulkiness and electron-attracting character of the R group. Later,[4] similar findings were obtained for $R=CH=CH_2$ and $R=C(Me)=CH_2$ (R^1 = i-Pr), *i.e.* for compounds containing a divinyl ether skeleton. These studies have now been extended to related systems containing a phenyl vinyl ether skeleton (*1* – *3*). In particular, this study is concerned with the effect of *o*-methyl substitution on the relative stabilities of the isomeric species *a* – *c*.

RESULTS AND DISCUSSION

Let us first consider the origin of the aforementioned dependence of the relative isomeric stability on the properties of R in reaction (1).[1-3] If the R group is not too bulky, the RO group assumes the planar s-*cis* conformation about the O – C(sp^2) bond in the *a* and *b* isomers (see below). This leads



a *b* *c* (1)

1, R = C_6H_5, R^1 = i-Pr; *2*, R = 2-$CH_3-C_6H_4$, R^1 = i-Pr; *3*, R = 2,6-$(CH_3)_2-C_6H_3$, R^1 = i-Pr.

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to unhindered p-π conjugation in the vinyloxy system:

$$-O-C=C \leftrightarrow -\overset{+}{O}=C-\overset{-}{C}$$

As a result of this electron delocalization, alkyl groups bound to the β carbon of the vinyl group do not stabilize the olefinic system as efficiently as they stabilize ordinary olefinic linkages in alkenes.[6] If, however, the extent of p-π conjugation in the vinyloxy system can be reduced, the double-bond character of the olefinic linkage is increased and the stabilizing power of R^1 in the *b* isomer approaches the value found in alkenes, which raises the stability of *b* relative to *a*. The decrease in the extent of p-π conjugation may be achieved by increasing the bulkiness of R, which forces the RO group to assume the nonplanar *gauche* structure shown above for *c*, or by increasing the electron-attracting nature of R.[2,5] On the other hand, the marked effect of the bulkiness of R on the relative stability of *c* may be rationalized as follows. Bulky R groups make any planar conformation (s-*cis* or s-*trans*) of the RO group inaccessible for the *a* and *b* forms, whereas the bulkiness of R has only an insignificant effect on the spatial structure of *c* (*gauche*). Thus with increasing bulkiness of R the energies of the *a* and *b* forms are increased relative to that of *c*.

Table 1 shows that the increasing steric requirements of the phenyl group due to *o*-methyl substitution *increase* the values of the thermodynamic parameters $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ for the $a \rightarrow b$, $a \rightarrow c$ and $b \rightarrow c$ reactions, relative the case R = phenyl. Thus it is evident that in *a* and *b* *o*-methyl substitution gives rise to such structures of the phenyl vinyl ether skeleton in which the extent of p-π conjugation in the vinyloxy group is increased relative to that in the corresponding isomer of *1*. The spectroscopic results (Tables 2 and 3) confirm this view: both the ^{13}C and ^{1}H NMR signals of the $=CH_2$ and $=CH$ moieties of *a* and *b* move upfield with increasing *o*-substitution, which points to increasing electron density around C-β and hence to enhancing conjugation in the vinyloxy goup in the sequence *1*–*2*–*3*. Related facts have been observed in diphenyl ethers: *o*-Substituents increase the conjugation between the O atom and the unsubstituted ring but decrease the conjugation between oxygen and the substituted phenyl group.[7] In the present compounds, conjugation in the ArO group is similarly decreased by *o*-substitution, *cf.* the $\delta(^{13}C$

Table 1. Thermodynamic data (cyclohexane solution, 298.15 K) for reaction (1) (R^1 = i-Pr). The errors are twice the standard errors.

Reaction	R	$\Delta G^{\ominus}$/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}
$a \rightarrow b$	C_6H_5 [a]	−0.85(0.04)	−1.1(0.2)	−0.7(0.6)
	2-Me-C_6H_4 [a]	0.12(0.03)	0.2(0.1)	0.1(0.3)
	2,6-diMe-C_6H_3 [a]	0.74(0.05)	1.0(0.2)	0.8(0.6)
	Me [b]	2.16(0.04)	0.0(0.2)	−7.1(0.6)
	$CH=CH_2$ [c]	−0.35(0.04)	−1.0(0.2)	−2.0(0.6)
	$C(Me)=CH_2$ [c]	−2.58(0.06)	−4.7(0.3)	−7.1(0.9)
$b \rightarrow c$	C_6H_5 [a]	−3.02(0.03)	−4.3(0.2)	−4.2(0.5)
	2-Me-C_6H_4 [a]	−1.96(0.03)	−3.2(0.2)	−4.2(0.4)
	2,6-diMe-C_6H_3 [a]	2.95(0.05)	2.7(0.2)	−1.0(0.5)
	Me [b]	6.92(0.04)	11.5(0.2)	15.2(0.5)
	$CH=CH_2$ [c]	−0.08(0.05)	0.6(0.2)	2.1(0.7)
	$C(Me)=CH_2$ [c]	−3.82(0.05)	−5.4(0.2)	−5.4(0.6)
$a \rightarrow c$	C_6H_5 [a]	−3.86(0.04)	−5.3(0.2)	−4.8(0.5)
	2-Me-C_6H_4 [a]	−1.85(0.04)	−3.1(0.2)	−4.1(0.4)
	2,6-diMe-C_6H_3 [a]	3.69(0.01)	3.6(0.1)	−0.2(0.1)
	Me [b]	9.10(0.06)	11.6(0.3)	8.4(0.8)
	$CH=CH_2$ [c]	−0.43(0.04)	−0.4(0.2)	0.1(0.5)
	$C(Me)=CH_2$ [c]	−6.39(0.09)	−10.1(0.5)	−12.4(1.1)

[a] This work. [b] Ref. 6. [c] Ref. 4.

Table 2. ^{13}C NMR chemical shift values ($CDCl_3$, $T = ca.$ 300 K) for the compounds studied in this work.

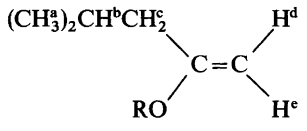
Comp.	C-1	C-2	C-3	C-4	C-5	*o*-Me	Aromatic carbons					
							C-1	C-2	C-3	C-4	C-5	C-6
1a	89.50	162.59	43.52	26.14	22.36		155.57	116.16	129.49	121.02	129.49	116.16
2a	86.99	161.91	43.75	26.14	22.42	15.90	154.13	131.09	126.80	121.65	?	?
3a	84.59	159.97	43.98	26.02	22.59	16.07	151.16	130.97	128.69	124.62	128.69	130.97
1b	14.70	147.79	120.28	26.88	23.45		156.76	117.87	129.43	122.11	129.43	117.87
2b	15.04	148.70	118.67[a]	26.88	23.68	16.07	153.28	131.09	126.91	122.97	?	?
3b	15.33	148.53	107.58	26.77	23.96	16.01	151.05	131.26	128.51	124.22	128.51	131.26
1c	18.24	145.04	124.16	24.94	23.05		156.65	116.16	129.49	121.48	129.49	116.16
2c	18.42	145.50	123.13	24.88	23.05	16.13	154.65	130.86	126.63	121.36	130.86	114.27
3c	18.30	146.99	113.87	24.48	23.28	16.36	151.16	131.27	128.40	124.00	128.40	131.27

[a] Assignment uncertain.

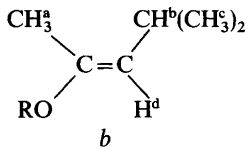
NMR) values of 121.02 and 124.62 for the *p*-carbon in *1a* and *3a*, respectively (if the conjugation were unaltered by the *o*-substituents, the latter shift value should be 0.2 ppm lower than the former[8]).

The most probable conformation of phenyl vinyl ether is shown in Fig. 1(a), where R = H. To maximize the extent of π-*p*-π conjugation, the molecule tends to achieve a completely planar structure ($\phi_1 = \phi_2 = 0°$), which trend is opposed by steric hindrance between R and one of the *o*-hydrogens so that in the energy minimum $\phi_1 = 50-60°$ and $\phi_2 = 10-20°$.[9] A minor amount of conformation (b) is also believed to be present.[10] Now when the α hydrogen (R) is replaced by a bulkier substituent, such as i-Bu (in *1a*), ϕ_1 and ϕ_2 in Fig. 1(a) are likely to widen and, moreover, the contribution of conformation

Table 3. ^1H NMR spectral data (CCl_4, TMS) for some aryloxy- and methoxy-substituted pentenes.



a



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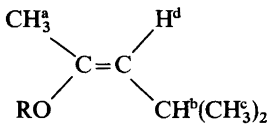

c

Compound	R	(a)	(b)	(c)	(d)	(e)	(*o*-Me)	(arom. H)	(MeO)	J_{bd}/Hz
1a	C_6H_5	1.00	?	2.09	3.87	4.03		6.7–7.4		
2a	2-Me-C_6H_4	1.00	?	2.09	3.58	3.85	2.14	6.5–7.1		
3a	2,6-diMe-C_6H_3	1.01	?	2.10	3.41	3.73	2.09	6.8		
	Me	0.94	?	1.94	3.70	3.75			3.54	
1b	C_6H_5	1.83	?	0.99	4.69			6.7–7.4		9.9
2b	2-Me-C_6H_4	1.87	?	0.93	4.29		2.14	6.5–7.1		9.4
3b	2,6-diMe-C_6H_3	1.92	?	0.85	3.73		2.07	6.8		9.1
	Me	1.74	?	0.91	4.05				3.45	8.6
1c	C_6H_5	1.74	?	0.93	4.76			6.7–7.4		9.4
2c	2-Me-C_6H_4	1.71	2.6	0.94	4.66		2.20	6.5–7.1		8.8
3c	2,6-diMe-C_6H_3	1.47	?	0.85	4.20		2.13	6.8		8.0

[a] The signal was not detected because of the strong splitting.

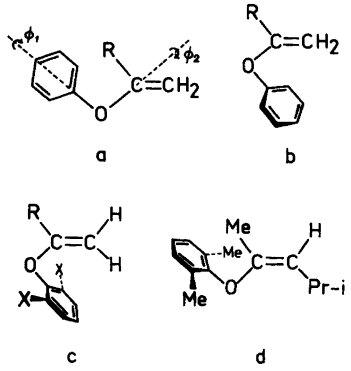

Fig. 1. Some possible conformations of phenyl vinyl ether and its derivatives.

(b) is probably increased because of the enhanced steric crowding between R and the aromatic ring [the $-CH_2-$ group of the i-Bu substituent, which has a direct steric interaction with the phenyl ring in conformation (a), has a van der Waals radius *ca.* 0.05 nm (0.5 Å) longer than that of an H atom[11]]. The increased contribution of (b) is verified by the ^{1}H NMR data: On going from phenyl vinyl ether to *1a*, the olefinic protons *trans* and *cis* to the PhO group are shielded by 0.46 and 0.63 ppm, respectively,[12] whereas in the corresponding structural change divinyl ether → α-isobutyl divinyl ether the shift values of the respective signals are decreased only by 0.22 and 0.43 ppm.[4] The higher shielding effect of the i-Bu group in *1a* thus points to an increased contribution of (b) in which the $=CH_2$ group lies in the shielding cone of the aromatic nucleus.[13]

The spectroscopic data provide interesting information also on the structures of the geometrical isomers *b* and *c*. In *a*→*b* [reaction (1)], the $\delta(^{13}C$ NMR) value of the β vinylic carbon increases from 81.38 to 104.93 ppm, *i.e.* by 23.6 ppm, if R = Me and R^1 = i-Pr.[14,15] For *1*, *2* and *3* the corresponding shift increments are 30.8, 31.7 and 23.0 ppm, respectively. Thus it appears that the *a*→*b* reaction involves similar (if any) changes in *p*-π conjugation in the O−C=C system when R = Me or R = 2,6-$(CH_3)_2-C_6H_3$ (*3*), whereas the extent of conjugation is decreased considerably if R = C_6H_5 (*1*) or R = 2-$CH_3-C_6H_4$ (*2*). The same trend is (although less clearly) also discernible in the $\delta(^1$H NMR) values of the olefinic proton *cis* to the ArO group: for *a*→*b* the shift changes are 0.66, 0.44 and 0.00 ppm for *1*, *2* and *3*, respectively, and 0.30 ppm for R = Me (see EXPERIMENTAL). These findings may be explained as follows. In *3a* and *3b* conjugation of the O atom with the aryl group is hindered by the *o*-substituents (*cf.* the corresponding derivatives of anisole[7,16] and phenyl vinyl ether[17]) and hence the O atom can conjugate effectively only with the C=C bond as in the corresponding derivatives of methyl vinyl ether. However, in *1a* and *2a* the maximum resonance stabilization is achieved when the O atom conjugates with both unsaturated moieties, although π-*p*-π orbital overlapping cannot be perfect on account of steric hindrance for planar systems. It has turned out, however, that π-electron distribution in conjugated systems like those in *1a* and *2a* is easily disturbed so that substitution of the olefinic hydrogens on C-β by alkyl groups may significantly decrease the ability of the substituted vinyl group to conjugate with the O atom, as previously shown for the structurally related divinyl ether system.[6,14] This probably arises from the electron-repelling character of the alkyl groups, which diminishes conjugation in the O−C=C system by opposing the accumulation of negative charge around C-β.

In the reaction *b*→*c* the $\delta(^1$H NMR) value of the Me group bound to C-α of the vinyl group decreases by 0.09 ppm for *1*, 0.15 ppm for *2* and 0.45 ppm for *3*. The low shift value of δ 1.47 for the Me group of *3c* suggests that this group lies in the shielding cone (*i.e.* above the plane) of the aromatic ring. In addition, the δ (^{13}C NMR) value of C-β of the vinyl group of *3c*, 113.87 ppm, is *ca.* 10 ppm lower than the corresponding shift values for *1c* and *2c* and, in fact, even lower than that (117.12 ppm[15]) for the case R = Me, R^1 = i-Pr. This shows that the extent of *p*-π conjugation in the O−C=C system of *3c* is high. Thus it seems appropriate to propose the structure shown in Fig. 1(d) for *3c*. The conformational change of the phenyl vinyl ether skeleton involved in the reaction *3b*→*3c* arises from the bulkiness of the i-Pr group, which makes the conformation of the reactant unfavorable for the product on account of heavy steric crowding between this group and the aromatic nucleus.

If R = Me in reaction (1), the *a*→*c* isomerization involves an s-*cis*→*gauche* change in the conformation of the MeO group, whereas no such reorientation of the RO group occurs if R is sufficiently bulky so that both the reactant and product assume the *gauche* structure. This appears to be the case when R = C(Me)=CH_2.[4,5] Hence the difference

in the values of $\Delta H^{\ominus}$ for R = Me and R = C(Me)= CH_2 should correspond to the energy required for the s-*cis*→*gauche* conformational change. For R^1 = i-Pr, the values of $\Delta H^{\ominus}$(g) of the *a*→*c* reaction are +12.2 and −10.9 kJ mol^{-1} for R = Me and R = C(Me) = CH_2, respectively.[4,6] Thus the enthalpy of the *gauche* form is obtained to be *ca.* 23 kJ mol^{-1} higher than that of the s-*cis* rotamer for R = Me. This agrees with theoretical calculations[18] proposing an enthalpy difference of 24−27 kJ mol^{-1} between the corresponding rotamers of methyl vinyl ether. Previously,[3] this enthalpy difference was estimated to be *ca.* 12 kJ mol^{-1} from the enthalpy change in the reaction (2), in which the 3-pentoxy

(*E*)-2-(3-pentoxy)-2-butene →
(*Z*)-2-(3-pentoxy)-2-butene (2)

group was believed to assume the *gauche* structure in the product as well as in the reactant. Despite the considerable bulkiness of the 3-pentyl group, it is obvious that a significant contribution of the s-*cis* form must, however, be present in the reactant since the value of $\Delta H^{\ominus}$(g) for this reaction, +1.9 kJ mol^{-1}, is markedly more positive than what might be expected from the magnitudes of the *cis* interaction energies in the reactant and product (S[Me···Me] = 4.2 and S[Me···O] = −2.9 kJ mol^{-1}).[19]

EXPERIMENTAL

Materials. The preparation of a mixture of *1a*−*1c* serves as an example of the synthetic method employed. Equivalent amounts of 2-methoxy-4-methyl-1-pentene[6] and phenol were mixed, some *p*-toluenesulfonic acid was added and the mixture was heated in a distillation apparatus until the evolution of MeOH ceased. The residue was washed several times with aqueous KOH to remove any unreacted phenol, dried (K_2CO_3) and distilled to give a liquid, b.p. 488−495 K at 102.0 kPa. The yield was 17 %. The isomeric forms of *2* and *3* were prepared similarly from 2-methylphenol and 2,6-dimethylphenol, respectively. The yields were low (5−10 %). Physical constants: *2* b.p. *ca.* 335 K at 0.4 kPa, *3* b.p. *ca.* 398 K at 0.8 kPa. For spectral characterization and the equilibrations pure compounds or mixtures of isomers with sufficiently different compositions were required, which was accomplished by fractionating the reaction products with a Perkin-Elmer M 250 Auto Annular Still.

^{13}C NMR spectra. The carbon spectra were recorded at 15 MHz in $CDCl_3$ with TMS as internal reference using a Jeol FT-60 NMR spectrometer. As an aid in signal assignment the shift data of Buchanan *et al.*[7] for some substituted diphenyl ethers were used. However, all the signals derived from the aromatic carbons of *2a* and *2b* and the signal of the *β* vinylic carbon of *2b* could not be assigned with certainty, since these compounds were not isolated as pure isomers but rather as a 50:50 mixture and, moreover, because the carbons concerned absorbed over a narrow spectral width. The carbon spectra are shown in Table 2.

^{1}H NMR spectra. The proton spectra were taken at 60 MHz in CCl_4 solution with TMS as internal reference. The spectrum of i-BuC(OMe) = CH_2 has been recorded previously[6] but the recording was repeated here under conditions of better resolution; hence the shift data given in Table 3 for the olefinic protons of this compound are slightly different from those reported earlier.

Equilibrations. Cyclohexane was used as solvent and I_2 as catalyst. The relative concentrations of the isomeric forms at equilibrium were determined by GLC using a Carbowax 20M column for *1* and *2* and an XE-60 column for *3*. The order of elution was *c*, *a*, *b* for *1*; *c*, *b*, *a* for *2* and *b*, *c*, *a* for *3*. Ten equilibration temperatures (287−425 K) were used for *1*, four for *2* (298−443 K) and four for *3* (298−393 K). In each case, the state of equilibrium was approached from two initial mixtures of isomers. The agreement between the relative equilibrium concentrations obtained from both initial mixtures was excellent. As an example, equilibration data for *2* are given below. T = 292.2 K: b/a = 0.949, c/a = 2.11, c/b = 2.22; T = 333.2 K: b/a = 0.965, c/a = 1.85, c/b = 1.92; T = 393.2 K: b/a = 0.964, c/a = 1.55, c/b = 1.60; T = 443.2 K: b/a = 0.972, c/a = 1.41, c/b = 1.45. The values of $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ at 298.15 K (Table 1) were obtained by a least-squares treatment of ln K against T^{-1}.

Configurational assignment. The configurations of the geometrical isomers were readily assigned from the ^{13}C NMR spectra: Previous studies[15] on the ^{13}C NMR spectra of a number of pairs of geometrical isomers like *b* and *c* in reaction (1) have revealed that the *b* form has the lower shift values for both the *β* vinylic carbon and the carbon bound to C-α of the vinyl group (= the C atom of the Me group in the present compounds). In addition, the ^{1}H NMR spectra and the values of the thermodynamic parameters are reasonable only if the configurations are taken as proposed by the carbon spectra.

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