

Thermodynamics of Vinyl Ethers. XXV.* Relative Stabilities of Some Methoxy Derivatives of 1,3- and 1,4-Pentadiene

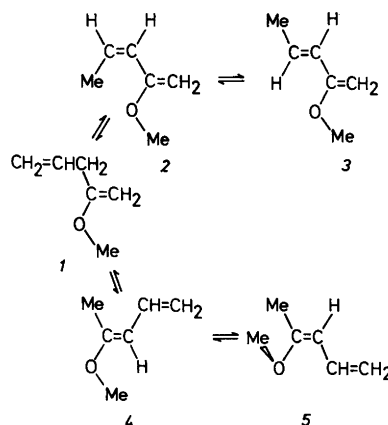
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The relative stabilities of 2-methoxy-1,4-pentadiene (1), (Z)-2-methoxy-1,3-pentadiene (2), (E)-2-methoxy-1,3-pentadiene (3), (E)-4-methoxy-1,3-pentadiene (4) and (Z)-4-methoxy-1,3-pentadiene (5) have been determined by chemical equilibration in cyclohexane solution at several temperatures. Within experimental error, the standard enthalpy of isomerization of 1 to 4 is equal to that involved in the reaction 1,4-pentadiene \rightarrow (Z)-1,3-pentadiene, which shows that the double-bond stabilizing power of a vinyl substituent in vinyl ethers (ca. 29 kJ mol⁻¹) is essentially equal to that in olefins although alkyl and phenyl groups are known to have a smaller stabilizing effect on the C=C bond of vinyl ethers than on that of olefins. In 2, steric interaction between the Me and C(OMe)=CH₂ groups gives rise to a *cis* strain of about 16 kJ mol⁻¹. Mesomerism and electron distribution in 4 and 5 are discussed on the basis of their carbon spectra.

Among the five isomeric pentadienes [1,2-pentadiene, 2,3-pentadiene, (E)- and (Z)-1,3-pentadiene and 1,4-pentadiene], the highest and lowest enthalpy contents are represented by the 1,2- and (E)-1,3-forms [ΔH_f^\ominus (g, 298 K) = 140.7 and 75.8 kJ mol⁻¹, respectively].¹ Thus the cumulated double bond system in the 1,2-isomer is 65 kJ mol⁻¹ less stable than the conjugated system of the (E)-1,3-form. Further, the 1,4-form with an isolated double bond system is 30 kJ mol⁻¹ less stable than the (E)-1,3-form, which is 4.2 kJ mol⁻¹ more stable than the corresponding (Z)-isomer.¹ The entropy difference between the geometrical isomers is small: ΔS^\ominus (g, 300 K) = $-(0.3 \pm 1.8)$ J K⁻¹ mol⁻¹ for the Z \rightarrow E reaction.²

* Part XXIV: Taskinen, E. *Acta Chem. Scand. B* 34 (1980) 203.



We now report the results of a thermodynamic study of the relative stabilities of the methoxy-substituted derivatives 1–5 of 1,3- and 1,4-pentadiene.

RESULTS AND DISCUSSION

The results of the equilibration experiments are shown in Tables 1 and 2. The values of ΔG^\ominus , ΔH^\ominus and ΔS^\ominus at 298.15 K were obtained from linear least-squares treatments of $\ln K$ against T^{-1} .

The reaction 1 \rightarrow 4 is highly exothermic with $\Delta H^\ominus(1) = -(29.2 \pm 1.8)$ kJ mol⁻¹. Since the normal boiling temperature of 4 is about 25 K higher than that of 1 (see EXPERIMENTAL), the standard enthalpy of vaporization (at 298 K) of liquid 4 is estimated³ to be 4.0 kJ mol⁻¹ more positive than that of liquid 1. Thus ΔH^\ominus (g, 298 K) = -25.2 kJ mol⁻¹ for 1 \rightarrow 4. This compares well with the

Table 1. Values of the mean equilibrium constant $K(x/y)$ for some selected reactions between the isomeric species 1–5.

T/K	$K(4/1)$	$K(3/2)$	$K(4/3)$	$K(4/5)$
443	127	13.5		
433	171	14.3	1.17	6.64
423	185	15.8	1.14	7.22
413	234	18.0	1.14	8.14
403	279	21.6	1.07	8.12
393	368	22.1	1.08	9.11
383	450			
373	591	29.7	1.02	10.9
353		40.0	1.00	13.8

enthalpy change in the related reaction 1,4-pentadiene \rightarrow (Z)-1,3-pentadiene [$\Delta H^\ominus(\text{g}) = -(25.6 \pm 1.8)$ kJ mol $^{-1}$ from the ΔH_f^\ominus -data given in Ref. 1]. Hence it may be concluded that the C=C bond of the vinyl ether 4 is stabilized by the vinyl (CH₂=CH) group to the same extent that the respective "ordinary" olefinic linkage in (Z)-1,3-pentadiene is stabilized by the vinyl group. This result is slightly unexpected, since alkyl and phenyl groups are known to have a weaker stabilizing effect on the olefinic system of vinyl ethers than on that of ordinary olefins.^{4,5}

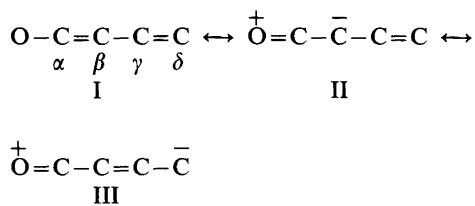
The observed enthalpy change for 1 \rightarrow 4 is a sum of the true double-bond stabilization energy of a vinyl group and the *cis* strain between the Me and vinyl groups in 4. The latter may be considered to be equal to the enthalpy change $\Delta H^\ominus(\text{g})$ in (E)-1,3-pentadiene \rightarrow (Z)-1,3-pentadiene, i.e. 4.2 kJ mol $^{-1}$ at 300 K.² Thus the true stabilization energy of a vinyl group linked to the olefinic system of vinyl ethers is obtained as (25.2 + 4.2) kJ mol $^{-1} \cong 29$ kJ mol $^{-1}$ (relative to that of a hydrogen atom). For comparison, the corresponding stabilization energy of a Ph group is only 15 kJ mol $^{-1}$.⁵

From the data of Table 2 for the 1 \rightarrow 4 and 3 \rightarrow 4 reactions, the value of $\Delta H^\ominus(\text{l})$ for 1 \rightarrow 3 is obtained as -32 kJ mol $^{-1}$, which is reduced to -29 kJ mol $^{-1}$ in the gas phase, since the normal boiling temperature of 3 is about 20 K higher than that of 1 (see EXPERIMENTAL) and hence the standard enthalpy of vaporization of 3 is 3 kJ mol $^{-1}$ higher than that of 1.³ The structural change in 1 \rightarrow 3 corresponds to that involved in the reaction 1,4-pentadiene \rightarrow (E)-1,3-pentadiene, for which $\Delta H^\ominus(\text{g}) = -(29.8 \pm 1.5)$ kJ mol $^{-1}$.¹ The enthalpy changes in these two analogous reactions are seen to be essentially equal.

The reaction enthalpy $\Delta H^\ominus(\text{l})$ for the reaction 2 \rightarrow 3 is markedly negative (-16.0 kJ mol $^{-1}$) pointing to a considerable steric repulsion between the Me and C(OMe)=CH₂ groups in the *cis* isomer (2). For comparison, the *cis* strain between the Me group and the unsubstituted vinyl group in (Z)-1,3-pentadiene is only 4.2 kJ mol $^{-1}$.² Thus it is obvious that the high strain in 2 may be ascribed to steric repulsion between the Me group and the O atom of the MeO group (the MeO group is likely to assume the *s-cis* conformation about the O–C_{sp²} bond; cf. the most stable conformation of methyl vinyl ether⁶). The entropy change $\Delta S^\ominus(\text{l})$ for 2 \rightarrow 3 (-15 J K $^{-1}$ mol $^{-1}$) is also unexpectedly negative in comparison with the negligible entropy change $\Delta S^\ominus(\text{g}) = -(0.3 \pm 1.8)$ J K $^{-1}$ mol $^{-1}$ in (Z)-1,3-pentadiene \rightarrow (E)-1,3-pentadiene.²

The isomerization 4 \rightarrow 5 involves replacing an Me-vinyl *cis* juxtaposition by an oxygen-vinyl *cis* juxtaposition with simultaneous rotation of the MeO group from the planar *s-cis* conformation to a nonplanar *gauche* conformation. Since Me-vinyl and Me-Me *cis* interaction energies are essentially equal (4.2 kJ mol $^{-1}$, Refs. 2 and 7), the enthalpy change in 4 \rightarrow 5 should correspond to that in the reaction (E)-2-methoxy-2-butene \rightarrow (Z)-2-methoxy-2-butene, if it is assumed that the Me-oxygen *cis* interaction energy in the product equals the vinyl-oxygen *cis* interaction energy in 5. In fact, the value of $\Delta H^\ominus(\text{l})$ for the latter reaction is (10.3 \pm 0.3) kJ mol $^{-1}$ (Ref. 4) to be compared with that (11.2 \pm 1.1 kJ mol $^{-1}$) for 4 \rightarrow 5. The entropy changes are also essentially equal (13.9 \pm 0.8 and 10.2 \pm 2.8 J K $^{-1}$ mol $^{-1}$, respectively).

The mesomeric structures I–III may be written



for 4. In comparison with vinyl ethers without an unsaturated substituent at the β carbon, the vinyl group of 4 gives rise to the additional mesomeric form III, which should decrease electron density on C- β but increase electron density on C- δ . Because of the wider separation of the positive and negative charges in III than in II, more energy is required

Table 2. Values of ΔG^\ominus , ΔH^\ominus and ΔS^\ominus at 298.15K for some selected reactions involving the species 1–5. The solvent is cyclohexane and the errors are twice the standard errors.

Reaction	$\Delta G^\ominus/\text{kJ mol}^{-1}$	$\Delta H^\ominus/\text{kJ mol}^{-1}$	$\Delta S^\ominus/\text{J K}^{-1} \text{mol}^{-1}$
1→4	-21.7(0.5)	-29.2(1.9)	-25(5)
2→3	-11.6(0.3)	-16.0(1.1)	-15(3)
3→4	0.5(0.2)	2.6(0.7)	7(2)
4→5	-8.2(0.3)	-11.2(1.1)	-10(3)

to produce ion III than ion II and hence the contribution of III to the real electronic structure should be smaller than that of II. This view is confirmed by the ^{13}C NMR spectrum of 4. If it is compared with that⁸ of the structurally analogous olefin, (Z)-1,3-pentadiene, it is observed that the β and δ carbons of 4 resonate 30.2 and 5.3 ppm upfield from those of the olefin, whereas the chemical shifts of the γ carbon are (within 1 ppm) equal in both compounds. These figures point to a marked increase in electron density around C- β and C- δ of the vinyl ether 4 but, according to expectation, the increase at C- β is not as pronounced as in vinyl ethers without an unsaturated substituent at this carbon. This becomes evident from the fact that in (Z)-2-butene and (Z)-4-methyl-2-pentene the replacement of the olefinic hydrogen at position 2 by an MeO group decreases^{8,9} the shift of C- β by 34.0 and 33.6 ppm, respectively. On going from 4 to 5, the chemical shifts of C- β and C- δ increase by 8.7 and 0.6 ppm, respectively, which reflects the decreased ability of the O atom in 5 to donate electrons to the unsaturated system through mesomerism. This shows that the planar *s-cis* conformation of the MeO group in 4 has changed to a nonplanar *gauche* structure in 5.⁹

EXPERIMENTAL

Materials. Methyl vinyl ether was slowly bubbled into a solution of bromine (1.3 mol) in dichloromethane (100 ml) until the color of bromine disappeared (the reaction mixture was cooled in an ice-bath). The product, methyl 1,2-dibromoethyl ether, was slowly dropped into an ice-cold solution of allylmagnesium chloride (1.3 mol) in ether (300 ml). After usual work-up, a 39% yield of 1-bromo-2-methoxy-4-pentene (b.p. 332–333 K at 2.0 kPa) was obtained. The product was dehydrobrominated by heating with KOH (70 g) in a distillation

apparatus. The organic layer of the distillate was separated and redistilled. The yield of 2-methoxy-1,4-pentadiene (1) was 38%, b.p. 366 K at 101.3 kPa. The other isomeric forms were obtained by dissolving 1 into a 3-fold volume of cyclohexane (0.004 M in I_2) and allowing the isomerization to proceed overnight. The solvent was removed at reduced pressure and the remainder was fractionated with a Perkin-Elmer M 251 Auto Annular Still. The 3, 4 and 5 forms could be isolated as practically pure liquids with the following boiling temperatures: 3 327 K at 12.0 kPa, 4 330 K at 12.0 kPa and 5 325 K at 9.3 kPa. On the other hand, the fraction containing isomer 2 was contaminated by appreciable amounts of 3 and some impurities. Thus only a few characteristic ^1H and ^{13}C NMR signals of 2 could be assigned with certainty in the spectra recorded on this fraction.

For the estimation of the standard enthalpies of vaporization at 298 K, the normal boiling temperatures of 3 and 4 were required. Since the normal boiling temperature of 2-methoxypropene (313 K¹⁰) is 28 K higher than that of methyl vinyl ether (285 K¹¹), the normal boiling temperature of 4 was similarly taken to be 28 K higher than that of 1-methoxy-1,3-butadiene (364–365 K¹¹), i.e. 392 K. Further, the difference in the normal boiling temperatures of 3 and 4 was assumed to be 3 K, the difference observed at a pressure of 12 kPa.

^1H NMR spectra (60 MHz, CCl_4 , δ values, coupling constants in Hz). 1: 5.6–6.3 (=CH), 5.20 (=CH, $J_{\text{cis}} \approx 6$), 5.06 (=CH, $J_{\text{trans}} \approx 13$), 3.86 (=CH₂), 3.54 (OMe), 2.83 (–CH₂–, $J_{\text{vic}} \approx 7$). 2: 5.5–5.8 (2 =CH), 3.86 (=CH₂), 3.50 (OMe), 1.85 (Me, $J_{\text{vic}} 5.2$). 3: 5.7 (2 =CH), 3.86 (=CH₂), 3.50 (OMe), 1.70 (Me, $J_{\text{vic}} 5.0$). 4: 6.2 (=CH), 5.12 (=CH, $J_{\text{vic}} 10.4$), 4.84 (=CH, $J_{\text{trans}} \approx 13$), 4.62 (=CH, $J_{\text{cis}} \approx 6$), 3.46 (OMe), 1.84 (Me). 5: 6.5 (=CH), 5.02 (=CH, $J_{\text{vic}} \approx 9$), 4.82 (=CH), 4.60 (=CH, $J_{\text{cis}} \approx 6$).

^{13}C NMR spectra (15 MHz, CDCl_3 , internal TMS, δ values). 1: 80.97 (C-1), 162.77 (C-2), 39.47 (C-3), 134.82 (C-4), 116.97 (C-5), 54.82 (OMe). 2: 85.86 (C-1, assignment uncertain), 128.38 (C-3), 125.74 (C-4), 15.02 (C-5), 54.41 (OMe, assignment uncertain). 3: 83.90 (C-1), 159.40 (C-2), 127.55 (C-3), 126.03 (C-4), 17.76 (C-5), 54.65 (OMe). 4: 110.81 (C-1), 133.17 (C-2), 100.30 (C-3), 157.29 (C-4), 16.63 (C-5), 54.31 (OMe). 5: 111.40 (C-1), 131.02 (C-2), 109.01 (C-3), 153.23 (C-4), 17.51 (C-5), 55.53 (OMe).

Equilibrations. The equilibration experiments were carried out in cyclohexane solution with I_2 as catalyst as described previously.³ The GLC analyses of the equilibrium mixtures were performed using a Carbowax 20 M column through which the isomeric species were eluted in numerical order. The state of equilibrium was approached from several initial mixtures of isomers at 9 temperatures between

353–443 K. The values of the equilibrium constant K for some selected reactions are seen in Table 1 and the values of ΔG^\ominus , ΔH^\ominus and ΔS^\ominus at 298.15 K in Table 2.

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Received April 4, 1980.