Tetrahedron Vol. 33, pp 2423 to 2427 Pergamon Press 1977 Printed in Great Britain

THERMODYNAMICS OF VINYL ETHERS—XXI†

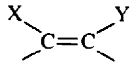
EVALUATION OF SOME *CIS* INTERACTION ENERGIES

E. TASKINEN* and M. ANTTILA
Department of Chemistry and Biochemistry, University of Turku, 20500 Turku 50, Finland

(*Received in the UK* 12 *January* 1977; *Accepted for publication* 24 *April* 1977)

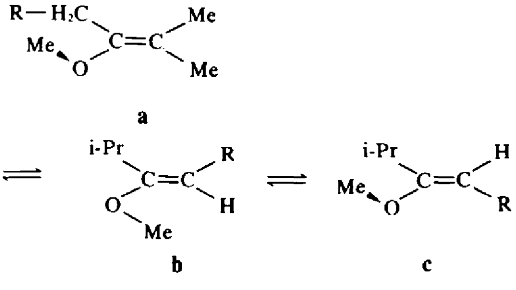
Abstract—Thermodynamics of isomerization reactions on some substituted vinyl methyl ethers have been studied for evaluating the magnitudes of the interaction energies S[R^1...R^2] between the substituents R^1 and R^2, juxtaposed in a *cis* position across the C=C bond of vinyl ethers. The results obtained are (values given in kJ mol^{-1}): S[Me...t-Bu] = 18.2 ± 1.0, S[Ph...i-Pr] = 11 ± 2, S[i-Pr...Et] = 6.1 ± 0.6, S[i-Pr...i-Pr] = 6.0 ± 0.6, S[O...t-Bu] = 2.9 ± 0.5, S[O...i-Pr] = −0.7 ± 0.5, S[O...Et] = −1.5 ± 0.5, S[O...Ph] = −2.1 ± 0.6, and S[O...Me] = −2.9 ± 0.2 (the symbol O stands for the ethereal oxygen atom of vinyl ethers). The negative interaction energy values reveal that the *cis* interaction between the ethereal oxygen and the alkyl (aryl) group concerned is stabilizing.

The present work aims at determining the values of the *cis* interaction energies S[X...Y] in the system



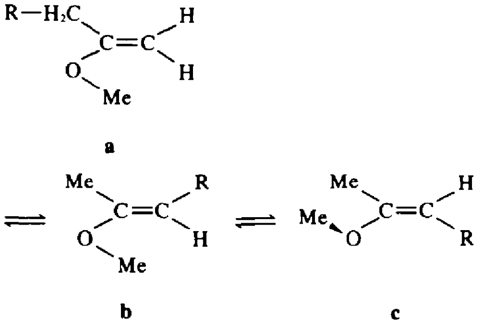
where X and Y are alkyl (aryl) groups, or X is an alkyl (aryl) group and Y the O atom of a MeO group. It should be particularly emphasized that in the latter case the term [O...X] involves only the interaction between the O atom and X, but *not* that between the MeO group and X, whose value depends on the spatial orientation (s-*trans* or gauche configuration about the O–C(sp^2) bond, see below) of the MeO group.

Experimentally, the work is based on determination of reaction enthalpies for suitable isomeric interconversions in which the groups of interest are juxtaposed in a *cis* position across the C=C bond. The reaction enthalpy thus involves the *cis* interaction energy. If the value of $\Delta H^{\ominus}$ of the same reaction can be estimated assuming no *cis* interaction, the *cis* interaction energy is evaluated from the difference between the experimental and estimated reaction enthalpies. The experimental reaction enthalpies were obtained from the temperature-dependence of the equilibrium constant. The following reactions have been studied:



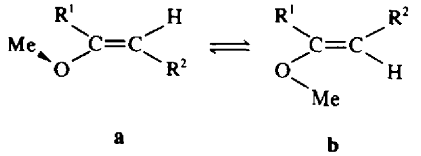
(1)

1: R = Et
2: R = i-Pr



(2)

3: R = t-Bu



(3)

4: R^1 = t-Bu, R^2 = Me
5: R^1 = Ph, R^2 = i-Pr
6: R^1 = R^2 = Ph

The thermodynamic data gained in the present work were combined with previous results of this series together with other literature data for evaluating the *cis* interaction energies.

RESULTS AND DISCUSSION

The results of the equilibration experiments are shown in Tables 1 and 2. The values of $\Delta H^{\ominus}$(g) and $\Delta S^{\ominus}$(g) (Table 2) were estimated from the corresponding liquid-phase data and the normal boiling temperatures as described previously.[1]

Starting with the i-Pr...R *cis* interaction energies, consider the thermodynamics of the **a**→**b** isomerization shown in reaction eqn (1). As supported by the following facts, the strain in the **a** isomer can be taken to be independent of R for R = Me, Et or i-Pr. Inspection of the most probable conformation of **2a** (R = i-Pr) along the i-Pr–CH_2 bond (I) reveals the existence of a Me...C(OMe)=CMe_2 gauche interaction, absent when

---

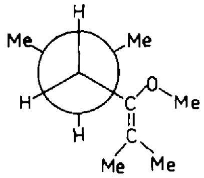
†Part XX: E. Taskinen and H. Lähteenmäki, *Finn. Chem. Lett.* in press.

Table 1. Thermodynamic data for the isomerization reactions studied in this work. The solvent is cyclohexane and temperature 298.15 K. The errors are twice the standard errors

Reaction	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
1a → **1b**	-0.28 ± 0.08	-5.6 ± 0.4	-17.9 ± 1.2
1a → **1c**	5.58 ± 0.22	5.3 ± 1.2	-1.0 ± 3.3
1b → **1c**	5.86 ± 0.24	10.9 ± 1.2	16.9 ± 3.5
2a → **2b**	1.04 ± 0.06	-5.3 ± 0.3	-21.2 ± 0.9
2a → **2c**	7.62 ± 0.06	7.3 ± 0.3	-1.2 ± 1.0
2b → **2c**	6.58 ± 0.09	12.5 ± 0.5	19.9 ± 1.4
3a → **3b**	12.72 ± 0.05	12.9 ± 0.3	0.6 ± 0.7
3a → **3c**	13.16 ± 0.07	15.8 ± 0.4	8.8 ± 1.1
3b → **3c**	0.43 ± 0.06	2.8 ± 0.3	8.0 ± 0.9
4a → **4b**	8.25 ± 0.05	6.4 ± 0.3	-6.3 ± 0.7
5a → **5b**	1.40 ± 0.12	-0.8 ± 0.9	-7.4 ± 2.6
6a → **6b**	2.38 ± 0.06	-3.6 ± 0.4	-20.0 ± 1.2

Table 2. Thermodynamic data (gas phase, 298.15 K) for the reactions studied in this work

Reaction	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
1a → **1b**	-7.1 ± 0.5	-19.6 ± 1.3
1a → **1c**	4.2 ± 1.3	-2.2 ± 3.4
1b → **1c**	11.3 ± 1.3	17.4 ± 3.6
2a → **2b**	-7.2 ± 0.4	-23.2 ± 1.0
2a → **2c**	5.9 ± 0.4	-2.7 ± 1.1
2b → **2c**	13.0 ± 0.6	20.4 ± 1.5
3a → **3b**	14.4 ± 0.4	2.4 ± 0.8
3a → **3c**	16.4 ± 0.5	9.5 ± 1.2
3b → **3c**	1.9 ± 0.6	6.9 ± 1.0
4a → **4b**	7.1 ± 0.4	-5.5 ± 0.9



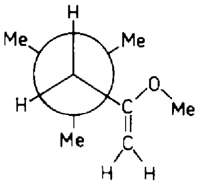
I

R = Me or Et. Energetically, this interaction is, however, negligible as shown by the following facts. The **a**→**b** isomerization given in reaction eqn (2) has been studied previously[2] for R = Me, Et and i-Pr with the results: R = Me, $\Delta H^{\ominus}(g) = 0.45 \pm 0.38$ kJ mol^{-1}; R = Et, $\Delta H^{\ominus}(g) = 0.78 \pm 0.39$ kJ mol^{-1}; R = i-Pr, $\Delta H^{\ominus}(g) = 0.60 \pm 0.37$ kJ mol^{-1}. Within experimental error, the $\Delta H^{\ominus}(g)$ values are equal. Since the *cis* strain S[Me...R] in the **b** isomer is the same (*ca.* 4.2 kJ mol^{-1}, see e.g. Ref. 3) for R = Me, Et and i-Pr, the equal $\Delta H^{\ominus}(g)$ values prove that also the **a** isomers are equally strained despite the Me... C(OMe)=CH$_2$ gauche interaction when R = i-Pr. In addition, it appears that the value of the Me... C(OMe)=CX$_2$ gauche interaction is the same for X = H and X = Me, since the CX$_2$ moiety probably projects away from the gauche Me group.

Another source of strain to be taken into account in the **a** isomer of reaction eqn (1) is the *cis* strain S[R–CH$_2$...Me]. However, it appears that the value of this interaction energy is essentially independent of R, since even in *cis*-dineopentylethylene the strain S[t-BuCH$_2$... CH$_2$Bu-t] is practically equal to that between the Me groups of *cis*-2-butene.[4]

Accordingly, it is concluded that the values of $\Delta H^{\ominus}(g)$ of the **a**→**b** isomerization shown in reaction eqn (1) do indeed reflect the relative strain energies S[i-Pr... R] (R = Me, Et and i-Pr) in the **b** isomer. As a standard reaction with known values of both $\Delta H^{\ominus}(g)$ and S[i-Pr... R] the case R = Me may be used. The value of S[i-Pr... Me] is taken[3,4] to be equal to S[Me... Me] (4.2 kJ mol^{-1}) and the value of $\Delta H^{\ominus}(g)$ is -9.03 ± 0.34 kJ mol^{-1} for R = Me.[1] Using the data of Table 2, the values of S[i-Pr... Et] and S[i-Pr... i-Pr] are now obtained as $4.2 + (-7.1 - (-9.03)) = 6.1$ and $4.2 + (-7.2 - (-9.03)) = 6.0$ kJ mol^{-1}, respectively. No literature data appear to exist for evaluating the former interaction energy but for the latter experimental data are found from two sources. First, the enthalpy of hydrogenation of *cis*-1,2-diisopropylethylene is 7.8 ± 0.3 kJ mol^{-1} more negative (more exothermic) than that of the *trans* isomer (acetic acid solution, 298 K).[4] Second, the enthalpy of combustion of the *cis* form is 8.2 ± 1.3 kJ mol^{-1} more negative than that of the *trans* form (liquid state, 298 K).[5] These data are not directly comparable with our results, since the literature data refer to the pure liquid olefins or their solution in acetic acid. On the other hand, calculations by the CFF method suggest the value of 6.5 kJ mol^{-1} for the gas-phase enthalpy difference between the *cis* and *trans* forms of 1,2-diisopropylethylene,[6] in good agreement with our experimental results.

The value of S[Me... t-Bu] is obtained from the enthalpy change in the **a**→**b** isomerization shown in reaction eqn (2). For R = Me $\Delta H^{\ominus}(g) = 0.45 \pm 0.38$ kJ mol^{-1},[2] and for R = t-Bu $\Delta H^{\ominus}(g) = 14.4 \pm 0.4$ kJ mol^{-1} (Table 2). Assuming the **a** isomers to be equally strained, S[Me... t-Bu] is obtained to be $14.4 - 0.45 \cong 14.0$ kJ mol^{-1} higher than S[Me...Me]. Considering the Newman projection of the most probable conformation of **3a** (R = t-Bu) along the t-Bu–CH$_2$ bond (II), two Me...C(OMe)=CH$_2$ gauche interactions are observed, but as explained above, these appear to be energetically negligible. Hence the value of S[Me...t-Bu] is obtained as $4.2 + 14.0 = 18.2$ kJ mol^{-1}. This may be compared with



II

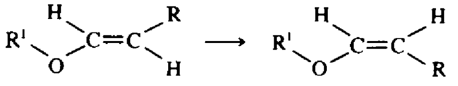
the value of $\Delta H^\ominus$ for the *trans* → *cis* isomerization of 4,4-dimethyl-2-pentene (1-Me-2-t-Bu-ethylene). This enthalpy change has been obtained as 17.9 ± 0.7 kJ mol^{-1} from the enthalpies of hydrogenation of the two isomers in acetic acid at 298 K,[7] and as 16.2 ± 2 kJ mol^{-1} from the enthalpies of combustion of the same compounds (gaseous state, see p. 154 of Ref. 3). According to CFF calculations, the enthalpy change in question should be 17.7 kJ mol^{-1}.[6] In this case it is questionable, however, whether the enthalpy difference between the *cis* and *trans* isomers equals the *cis* strain, since even the *trans* isomer has been estimated to be strained by *ca.* 7 kJ mol^{-1}.[8] If this is accepted, **3a** is also strained by approximately the same amount, which seems unlikely in view of the discussion above.

The Me...t-Bu *cis* interaction is also present in **4b**. The value of $\Delta H^\ominus$(g) for **4a**→**4b** is *ca.* 17.0 kJ mol^{-1} more positive than that (−9.85 ± 0.41 kJ mol^{-1}, Ref. 2) for the related reaction with $R^1 = R^2 =$ Me. Thus the value of S[Me...t-Bu] should be *ca.* 4.2 + 17.0 = 21.2 kJ mol^{-1}. However, this result is acceptable only if the strain in the **a** isomer is the same for R^1 = t-Bu or Me, which is not easily proved.

The term S[Ph...i-Pr] may be evaluated as follows. The value of $\Delta H^\ominus$(l) of reaction **5a**→**5b** is 1 kJ mol^{-1} less negative than that (−1.8 ± 0.8 kJ mol^{-1}, Ref. 9) of the related reaction with R^1 = Ph and R^2 = Me. This value (1 kJ mol^{-1}) does not, however, represent the difference between Ph...i-Pr and Ph...Me *cis* strain energies, since the O...R^2 *cis* interaction in the **a** isomer is *ca.* 2.2 kJ mol^{-1} less stabilizing for R^2 = i-Pr than R^2 = Me (see below). If the value of S[Ph...Me] is taken as suggested previously[10] (7.5 ± 1.5 kJ mol^{-1}), S[Ph...i-Pr] is obtained as 7.5 + 1 + 2.2 = 11 kJ mol^{-1}.

Reaction **6a**→**6b** deserves special attention. The reaction enthalpy $\Delta H^\ominus$(l) is *ca.* 1.8 kJ mol^{-1} more negative than that (−1.8 kJ mol^{-1}, Ref. 9) of the related reaction with R^1 = Ph and R^2 = Me. As will be shown later in this paper, the O...R^2 *cis* interaction in the **a** isomer is *ca.* 0.8 kJ mol^{-1} less stabilizing for R^2 = Ph than R^2 = Me. Thus the value of S[Ph...Ph] would be 1.8 − 0.8 = 1 kJ mol^{-1} *less* than that of *S*[Ph...Me]. This is in considerable disagreement with expectation: as discussed previously,[10] the Ph...Ph *cis* strain in *cis*-stilbene (1,2-diphenylethylene) is 12–16 kJ mol^{-1} (taken to be equal to the difference in the standard enthalpies of the gaseous *cis* and *trans* isomers), whereas the term S[Ph...Me] was evaluated as 7.5 ± 1.5 kJ mol^{-1}.[10] Clearly, the value of S[Ph...Ph] cannot be estimated correctly by the method used above, which is explainable as follows. Considering the **a** isomer of reaction eqn (3), the C atom of the MeO group cannot lie in the plane of the C=C bond, if R^1 and R^2 are bulkier than a hydrogen atom, i.e. the MeO group is forced to assume a nonplanar gauche configuration. This leads to decreased conjugation between the lone electron pairs of the O atom and the π electrons of the C=C bond. Now if R^2=Ph, conjugation may extend from the Ph group to the ethylenic bond but not to the O atom, whereas in the **b** isomer a long conjugated system from the Ph to the MeO group is possible, which leads to the enhanced stability. The high decrease in entropy (−20 J K^{-1} mol^{-1}) on going from **6a** to **6b** suggests that the presence of two Ph groups in a *cis* position strongly restricts their rotation about the Ph–vinyl bond (cf. $\Delta S^\ominus$(l) = −1.15 ± 2.5 J K^{-1} mol^{-1} for the related reaction with R^1 = Ph and R^2 = Me, Ref. 9). Since both Ph groups of the **b** isomer cannot be coplanar with the ethylenic system because of steric crowding (cf. the structure of *cis*-stilbene[12–15]), it appears that the β Ph group assumes a coplanar arrangement with the C=C bond for maximum conjugation, whereas the α Ph group is tilted out of coplanarity.

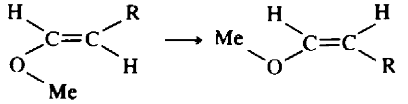
Next let us consider the O...R *cis* interactions S[O...R]. For R = Me, the value of this interaction may be equated with the enthalpy change $\Delta H^\ominus$(g) of reaction 4 (R = Me) in cases where the R^1O group is not rotated



(4)

about the O–C(sp^2) bond during the reaction (i.e. both the product and reactant exist in the s-*trans* configuration). This situation is encountered in the following cases ($\Delta H^\ominus$(g) in kJ mol^{-1} given in parentheses): R^1 = t-Bu (−2.9),[11] MeCH=CH (−2.6),[16] EtCH=CH (−3.3),[16] i-PrCH=CH (−3.1),[16] and Me$_2$C=CH (−2.7),[16] On average, $\Delta H^\ominus$(g) = S[O...Me] = −2.9 kJ mol^{-1}, i.e. the O...Me *cis* interaction is *stabilizing* by 2.9 kJ mol^{-1}.

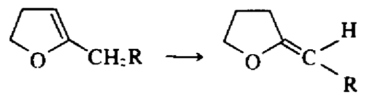
The value of S[O...Et] is obtained as follows. First, when R = Et and R^1 = MeCH=CH in reaction 4, $\Delta H^\ominus$(g) = −2.2 kJ mol^{-1},[16] which may be equated with S[O...Et]. Second, the values of $\Delta H^\ominus$(g) of reaction (5) are 0.4 and 2.2 kJ mol^{-1},[11,16] respectively, for R = Me and R = Et.



(5)

Thus S[O...Et] − S[O...Me] = 1.8 kJ mol^{-1}, and hence S[O...Et] = −2.9 + 1.8 = −1.1 kJ mol^{-1}. Third, the values of $\Delta H^\ominus$(g) of the **a**→**c** isomerization shown in reaction eqn (1) are 2.6 and 4.2 kJ mol^{-1} for R = Me (Ref. 1) and R = Et (this work), respectively. It follows that S[O...Et] is 1.6 kJ mol^{-1} less stabilizing than S[O...Me], i.e. S[O...Et] = −1.3 kJ mol^{-1}. The average of these three estimates is S[O...Et] = −1.5 kJ mol^{-1}.

The term S[O...i-Pr] may be evaluated from the following reaction enthalpies. First, when R = i-Pr and R^1 = MeCH=CH in reaction eqn (4), $\Delta H^\ominus$(g) = −1.7 kJ mol^{-1},[16] which may be equated with S[O...i-Pr]. Second, the values of $\Delta H^\ominus$(g) of reaction (5) depend on R as follows: R = Me, $\Delta H^\ominus$(g) = 0.4 kJ mol^{-1} (Ref. 11) and R = i-Pr, $\Delta H^\ominus$(g) = 3.3 kJ mol^{-1} (Ref. 16). The difference between these reaction enthalpies is 2.9 kJ mol^{-1} and hence S[O...i-Pr] = 0.0 kJ mol^{-1}. Third, for the **a**→**c** isomerization shown in reaction eqn (2) the values of $\Delta H^\ominus$(g) are 10.3 and 12.2 kJ mol^{-1},[2] respectively, for R = Me and R = i-Pr. Accordingly, S[O...i-Pr] = −2.9 + (12.2 − 10.3) = −1.0 kJ mol^{-1}. Fourth, reaction 6 was studied previously[17] with the results $\Delta H^\ominus$(g) = 0.1 kJ mol^{-1} for R = Me and 2.0 kJ mol^{-1} for R = i-Pr. It follows that S[O...i-Pr] = −1.0 kJ mol^{-1}. Fifth,

 (6)

$\Delta H^{\ominus}(g) = 2.6$ kJ mol^{-1} for R = Me[1] and 5.9 kJ mol^{-1} for R = i-Pr (this work) for the **a**→**c** interconversion shown in reaction equation 1. Thus S[O ... i-Pr] = 0.4 kJ mol^{-1}. On average, S[O ... i-Pr] = −0.7 kJ mol^{-1}.

The O ... t-Bu *cis* interaction energy may be evaluated from the enthalpy changes for the **a**→**c** isomerization shown in reaction equation (2): R = Me, $\Delta H^{\ominus}(g) =$ 10.3 kJ mol^{-1} (Ref. 2) and R = t-Bu, $\Delta H^{\ominus}(g) =$ 16.4 kJ mol^{-1} (this work). Hence S[O ... t-Bu] = −2.9 + 6.1 = 3.2 kJ mol^{-1}. Another estimate of the same quantity may be obtained from the $\Delta H^{\ominus}(l)$ data reported by Okuyama *et al.*[18] for reaction 4 with R^1 = Et: $\Delta H^{\ominus}(l) =$ 1.6 kJ mol^{-1} for R = Me and 7.0 kJ mol^{-1} for R = t-Bu. Thus S[O ... t-Bu] = 2.5 kJ mol^{-1}. On average, S[O ... t-Bu] = 2.9 kJ mol^{-1} (destabilizing).

Finally, the value of S[O...Ph] is derived from the enthalpy data for reaction 5: R = Me, $\Delta H^{\ominus}(g) =$ 0.4 kJ mol^{-1} (Ref. 11) and R = Ph, $\Delta H^{\ominus}(g) = 1.2$ kJ mol^{-1} (Ref. 10). Accordingly, S[O...Ph] = −2.1 kJ mol^{-1}.

The results of the present study are summarized in Table 3, which shows the values of the *cis* interaction energies in the order of decreasing destabilization between the interacting moieties.

Table 3. Values of some *cis* interaction energies across the C=C bond of vinyl ethers. Positive values denote destabilizing, negative values stabilizing interactions between the groups R^1 and R^2. The errors are estimated errors

R^1	R^2	$S[R^1 \cdots R^2]$/kJ mol^{-1}
Me	t-Bu	18.2 ± 1.0 [a]
Ph	i-Pr	11 ± 2 [b]
i-Pr	Et	6.1 ± 0.6 [a]
i-Pr	i-Pr	6.0 ± 0.6 [a]
O	t-Bu	2.9 ± 0.5
O	i-Pr	−0.7 ± 0.5
O	Et	−1.5 ± 0.5
O	Ph	−2.1 ± 0.6
O	Me	−2.9 ± 0.2

[a] Based on the value of S[Me···Me] = 4.2 kJ mol^{-1}. [b] Based on the value of S[Ph···Me] = 7.5 kJ mol^{-1}.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded in CCl_4 at 60 MHz with TMS as internal reference. The chemical shifts are shown in τ value (ppm) and the coupling constant in Hz. In many cases the spectra were taken on mixtures of isomers, since pure isomers could not always be isolated, usually due to their low concentration in the synthetic mixture. The NMR signals of **3b**, **3c** and **4b** were not detected for the same reason. The vinyl ethers were prepared by the route amply illustrated in the previous parts of this series: ketone → acetal → vinyl ether. Preparative GLC was used for separating the components of the synthetic mixtures (the column was a Carbowax 20 M column).

Compound **1**. From isopropyl n-propyl ketone and trimethyl orthoformate.[19] yield 76% boiling temp. (b.t.) 403–405 K at 102.2 kPa. NMR: **1a**, 6.64 (MeO), 7.91 ($-CH_2-C{=}C$, J_{vic} 6.8), 8.4 ($Me_2C{=}C$), 8.7 (CH_2), 9.11 (Me, J 6.9). **1b**, 5.88 (H–C=C, J_{vic} 7.1), 6.59 (MeO), 7.27 ($H{-}C\overset{\diagup}{\underset{\diagdown}{-}}$, J_{vic} 6.8), 8.01 (CH_2, J_{vic} 7.1), 9.01 (Me of the i-Pr group, J 6.9), 9.05 (Me of the Et group, J 6.8). **1c**, 5.53 (H–C=C, J_{vic} 6.8), 6.51 (MeO), 7.8 ($H{-}C\overset{\diagup}{\underset{\diagdown}{-}}$), 7.96 ($CH_2$), 9.00 (Me of the i-Pr group, J 6.9), 9.05 (Me of the Et group, J 6.8).

Compound **2**. From isobutyl isopropyl ketone and trimethyl orthoformate. Yield 77%, b.t. 416–421 K at 101.3 kPa. NMR: **2a**, 6.65 (MeO), 7.9–8.2 ($CH_2{-}CH\langle$), 8.40 (Me–C=C), 8.44 (Me–C=C), 8.44 (Me–C=C), 9.14 (Me, J 6.2). **2b**, 6.02 (H–C=C, J 9.4), 6.60 (MeO), 7.28 (methine proton of the α i-Pr group, J 6.9), 7.3–7.8 (methine proton of the β i-Pr group), 9.01 (Me, J 6.8), 9.05 (Me, J 6.8). **2c**, 5.66 (H–C=C, J_{vic} 9.3, $J_{allylic}$ 0.9), 6.51 (MeO), 7.0–8.2 (methine protons of the i-Pr groups), 9.00 (Me, J 6.9), 9.09 (Me, J 6.9).

Compound **3**. From methyl neopentyl ketone and trimethyl orthoformate. Yield 59%, b.t. 395 K at 101.3 kPa. NMR: **3a**, 6.16 (H–C=C, J_{gem} 1.5), 6.28 (H–C=C), 6.56 (MeO), 8.06 (CH_2), 9.09 (Me).

Compound **4**. From t-butyl ethyl ketone and trimethyl orthoformate. The acetal was formed very slowly: the reaction mixture was kept at RT for 6 months, after which only *ca.* 30% of the ketone had reacted. A 20% yield of mainly **4a**, b.t. *ca.* 395 K at 101.3 kPa, was obtained. NMR: **4a**, 5.33 (H–C=C, J_{vic} 6.9), 6.40 (MeO), 8.44 (Me–C=C, J_{vic} 6.9), 8.99 (Me).

Compound **5**. From isobutyl phenyl ketone and trimethyl orthoformate. Yield 89%, b.t. 339–342 K at 0.3 kPa. NMR: **5a**, 2.7 (aromatic protons), 4.99 (H–C=C, J_{vic} 9.3), 6.55 (MeO), 8.96 (Me, J 6.7). **5b**, 2.7 (aromatic protons), 5.57 (H–C=C, J_{vic} 10.3), 6.46 (MeO), 9.01 (Me, J 6.7). The strongly splitted signals of the methine protons of both isomers were found at τ 6.8–7.8.

Compound **6**. From benzyl phenyl ketone and trimethyl orthoformate. Yield 80%, b.t. 410–417 K at 0.4 kPa. MNR: **6a**, 4.01 (H–C=C), 6.46 (MeO). **6b**, 4.31 (H–C=C), 6.31 (MeO). The aromatic protons of **6a** and **6b** absorbed at 2.2–3.1.

Configurational assignments. The configurations of the geometric isomers of **1**, **2**, **5** and **6** were readily assigned from the relative ^{1}H NMR shift values of their olefinic protons. As shown previously for structurally related compounds,[1,9,10] the olefinic proton of the Z isomer (configurationally similar to **1c**, **2c**, **5a** and **6a**) absorbs *ca.* 0.3–0.5 ppm downfield from that of the E form. The configurations of the geometric isomers of **3** and **4** could be assigned from their relative boiling temperatures: if the normal b.t.'s of alkylsubstituted vinyl methyl ethers are compared with those of the corresponding olefins (i.e. compounds in which the MeO group of a vinyl ether has been replaced by an H atom), the relative b.t.'s of the isomeric compounds are found to be similarly dependent on structure. For example, the normal b.t.'s of 1-butene, *cis*- and *trans*-2-butene are 266.9, 276.9 and 274.1 K,[20] respectively, and those of the structurally analogous vinyl ethers 2-MeO-1-butene, (E)-2-MeO-2-butene and (Z)-2-MeO-2-butene 338.4, 352.2 and 349.7 K,[2] respectively. Similarly, the normal b.t.'s of the olefins corresponding to **3a**, **3b** and **3c** are 345.7, 353.6 and 350.0 K,[20] respectively, and since the b.t.'s of the geometric isomers of **3** are (see below) 398.7 and 392.9 K, the higher value should be ascribed to the E structure (**3b**). The same principle was applied for determining the configurations of the geometric isomers of **4**.

Support for the configurational assignments described above is obtained from the thermodynamic data. As shown previously for the interconversion of structurally related geometric isomers (see, e.g. Refs. 1, 2, 9 and 10), the entropy change is always positive for the E→Z isomerization (**b**→**c** for **1**–**3** and **b**→**a** for **4**–**6**). Moreover, the reaction enthalpies are reasonable only if the configurations are taken as proposed above (exception: compound **6**, in which the situation is less unambiguous).

Determination of normal boiling temperatures. The gas-chromatographic method described previously[1] was used with the results shown below (b.t. in K at 101.325 kPa): **1a**, 409.7; **1b**, 400.2; **1c**, 402.9; **2a**, 417.7; **2b**, 406.2; **2c**, 409.0; **3a**, 389.2; **3b**, 398.7; **3c**, 392.9; **4a**, 398.7; **4b**, 403.2. The b.t.'s of **5** and **6** were not determined in the absence of suitable high-boiling reference compounds.

Equilibrations. The equilibrations were carried out in cyclohexane solution with I_2 as catalyst.[21] The total substrate concentration was 20% (v/v). The substrates used for the equilibrations were: pure **a** and pure **b** isomers for **1** and **2**, pure **a** for **3** and **4**, two mixtures of **a** and **b** for **5** (I, **a**:**b** = 1.73; II, **a**:**b** = 2.81)†. In the case of **3** and **4**, the equilibrium mixture was thus approached from one starting mixture only, since the synthetic route employed gave only one of the two or three isomers in isolable amounts. However, according to our experience on related compounds, the same equilibrium mixture is readily achievable from any starting composition and, in addition, plots of the equilibrium constant against temperature obeyed nicely the van't Hoff equation, and thus the results reported seem trustworthy. Prior to analysis, the equilibrium mixtures were made alkaline by adding a small amount of diethylamine.[21] The equilibrated samples of **1**–**4** were analyzed by GLC using a Carbowax 20 M column and those of **5** and **6** by ^{1}H NMR from the relative integrated intensities of the MeO signals. The NMR method was used for the latter compounds because **5a** and **5b** were not sufficiently separated by the gas-chromatographic columns available to us and because compound **6** was too high-boiling for reliable (isomerization-free) GLC analysis. The order of elution through the Carbowax 20 M column was **b**, **c**, **a** for **1** and **2**, **a**, **c**, **b** for **3**, and **a**, **b** for **4**. The temperatures covered by the experiments were: **1**: 300, 323, 378 and 403 K; **2**: 300, 323, 373 and 403 K; **3**: 15 temperatures from 283 to 417 K; **4**: 300, 333, 373 and 403 K **5**: 300, 323, 347 and 375 K; **6**: 300, 323, 348 and 374 K. The errors of the thermodynamic parameters were estimated as described previously.[1]

REFERENCES

[1] E. Taskinen, *J. Chem. Thermodyn.* **6**, 271 (1974).

[2] E. Taskinen, *Ibid.* **6**, 345 (1974).

[3] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, pp. 142, 146, 150, 579. Academic Press, New York (1970).

[4] R. B. Turner, A. D. Jarrett, P. Goebel and B. J. Mallon, *J. Am. Chem. Soc.* **95**, 790 (1973).

[5] K. Yates and R. S. McDonald, *Ibid.* **93**, 6297 (1971).

[6] O. Ermer and S. Lifson, *Tetrahedron* **30**, 2425 (1974).

[7] R. B. Turner, D. E. Nettleton, Jr. and M. Perelman, *J. Am. Chem. Soc.* **80**, 1430 (1958).

[8] H. A. Skinner, *J. Chem. Soc.* 4396 (1962).

[9] E. Taskinen and E. Mustonen, *Acta Chem. Scand.* **B30**, 1 (1976).

[10] E. Taskinen and P. Ylivarinio, *Ibid.* **B29**, 1 (1975).

[11] E. Taskinen and P. Liukas, *Ibid.* **B28**, 114 (1974).

[12] D. L. Beveridge and H. H. Jaffe, *J. Am. Chem. Soc.* **87**, 5340 (1965).

[13] H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules*, p. 306. Academic Press, New York (1967).

[14] M. Traetteberg and E. B. Frantsen, *J. Mol. Struct.* **26**, 69 (1975).

[15] F. Heatley, M. K. Cox, A. Jones and B. Jacques, *J. Chem. Soc.* Perkin Trans. **2**, 510 (1976).

[16] E. Taskinen and R. Virtanen, *J. Org. Chem.* **42**, 1443 (1977).

[17] E. Taskinen, *Acta Chem. Scand.* **B29**, 245 (1975).

[18] T. Okuyama, T. Fueno and J. Furukawa, *Tetrahedron* **25**, 5409 (1969).

[19] H. O. House and V. Kramar, *J. Org. Chem.* **28**, 3362 (1963).

[20] *Physical Properties of Chemical Compounds-II.* American Chemical Society, Washington, D.C. (1959).

[21] E. Taskinen, *J. Chem. Thermodyn.* **5**, 783 (1973).

---

†Similarly for **6** (I, **a**:**b** = 3.26; II, **a**:**b** = 0.86)