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THERMODYNAMICS OF VINYL ETHERS—XVIII†

UNSATURATED ACETALS

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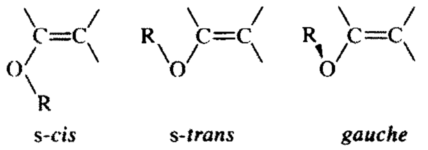
Abstract—A thermodynamic study of geometrical isomerization reactions of unsaturated acetals $R^1R^2C(OCH{=}CHMe)_2$ and $MeOC(R^1R^2)OCH{=}CHMe$ is reported. The values of the thermodynamic parameters of isomerization are rather insensitive to the bulkiness of R^1 and R^2 suggesting that the favored rotamers of these acetals are not the s-*cis* but the s-*trans* rotamers. This conclusion is supported by IR and NMR data.

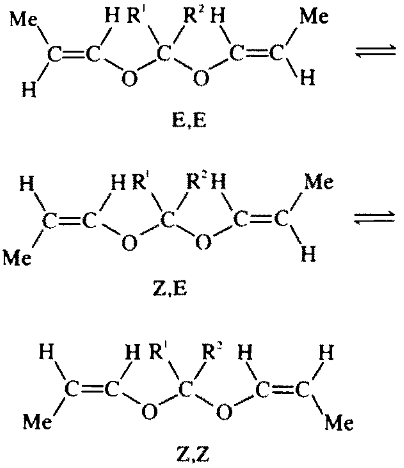
The relative stability of the E and Z forms of alkyl propenyl ethers ($ROCH{=}CHMe$) has been shown[1] to depend considerably on the bulkiness of the alkyl group. For example, for the E → Z reaction the values of $\Delta H^\ominus(1)$ and $\Delta S^\ominus(1)$ are as follows: R = Me, $\Delta H^\ominus = 1.26 \pm 0.12$ kJ mol^{-1} and $\Delta S^\ominus = 4.09 \pm 0.35$ J K^{-1} mol^{-1}; R = t-Bu, $\Delta H^\ominus = -2.08 \pm 0.11$ kJ mol^{-1} and $\Delta S^\ominus = 6.29 \pm 0.31$ J K^{-1} mol^{-1}.[1] The dependence of $\Delta H^\ominus$ and $\Delta S^\ominus$ on R is a consequence of rotational isomerism about the O–C(sp^2) bond in these ethers.[1] In the case of a small alkyl group (such as Me), the E isomer exists mainly in the low-energy planar s-*cis* configuration (Scheme 1).



Scheme 1.

As the size of the alkyl group increases, the s-*cis* rotamer becomes less favored because of steric crowding in this arrangement, and the proportion of the other possible (s-*trans* and/or gauche) rotamers increases. For a sufficiently bulky alkyl group the s-*cis* rotamer is no more possible. For the Z isomer the s-*cis* configuration is also excluded, independent of the bulkiness of R. Hence in the case of a small alkyl group the E → Z reaction involves energy-demanding changes in the configuration of the alkoxy group, whereas the spatial orientation of the alkoxy group apparently remains unchanged, if the alkyl group is sufficiently bulky (such as t-Bu).

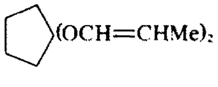
The aim of the present work was to clarify whether the bulkiness of the groups R^1 and R^2 of the following unsaturated acetals has any effect on the thermodynamics of their isomeric interconversion. For the E,E isomer of **1**, the planar s-*cis*, s-*cis* structure (Scheme 2) is not excluded by steric factors, whereas the planar s-*trans*, s-*trans* (or the nonplanar gauche) structures seem more probable for the E,E isomers of **5** and **6** as well as for all Z,Z isomers, independent of the bulkiness of R^1 and R^2. Thus it appears that if the values of $\Delta H^\ominus$ and $\Delta S^\ominus$ of the E,E → Z,Z reactions of **1–6** (E → Z reactions of **7–9**) are independent of R^1 and R^2, none of these compounds exists in the s-*cis*, s-*cis* or s-*cis*, s-*trans* (**1–6**) or s-*cis* (**7–9**) configurations.

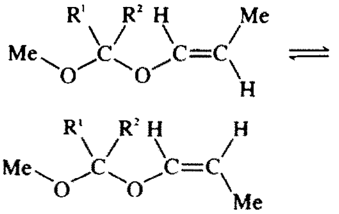


(1)

1: $R^1 = R^2 = H$
2: $R^1 = H$, $R^2 = Me$
3: $R^1 = H$, $R^2 = i\text{-}Pr$
4: $R^1 = H$, $R^2 = t\text{-}Bu$
5: $R^1 = R^2 = Me$

6:





(2)

7: $R^1 = R^2 = H$
8: $R^1 = H$, $R^2 = Me$
9: $R^1 = R^2 = Me$

The two oxygen atoms of **1–9** are separated by one carbon atom. For comparison, the E → Z reaction of **10**, in which the oxygen atoms are separated by two carbon atoms, was studied:

$$\underset{\mathbf{10E}}{(E)\text{-}MeOCH_2CH_2OCH{=}CHMe} \rightleftharpoons \underset{\mathbf{10Z}}{(Z)\text{-}MeOCH_2CH_2OCH{=}CHMe} \quad (3)$$

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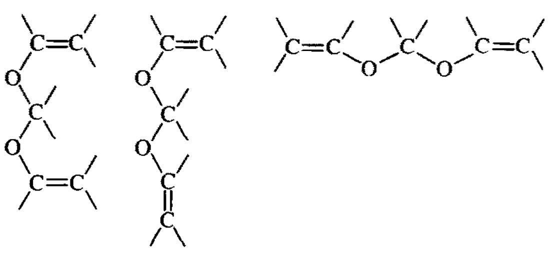
†Part XVII, E. Taskinen, preceding paper.



Scheme 2.

Table 1. Thermodynamic data for the isomerization reactions studied in this work. Neat liquid, 298.15 K. The errors are twice the standard errors, unless otherwise noted

Reaction	Comp.	$\Delta G^{\ominus}$/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}
E,E→Z,E	1	−3.66 ± 0.03	−2.0 ± 0.2	5.6 ± 0.5
	2	−4.10 ± 0.04	−1.9 ± 0.2	7.3 ± 0.7
	3	−4.42 ± 0.04	−2.9 ± 0.2	5.1 ± 0.7
	4	−4.87 ± 0.12	−2.3 ± 0.7	8.7 ± 2.0
	5	−4.7 ± 0.2^{a}	...	...
	6	−4.5 ± 0.2^{a}	...	...
Z,E→Z,Z	1	−0.40 ± 0.05	−2.0 ± 0.3	−5.3 ± 0.8
	2	−0.76 ± 0.05	−2.0 ± 0.3	−4.2 ± 0.8
	3	−1.07 ± 0.08	−2.3 ± 0.4	−4.0 ± 1.4
	4	−1.38 ± 0.04	−2.3 ± 0.2	−3.1 ± 0.7
	5	−0.9 ± 0.1^{a}	...	...
	6	−0.9 ± 0.1^{a}	...	...
E,E→Z,Z	1	−4.06 ± 0.03	−4.0 ± 0.2	0.3 ± 0.4
	2	−4.86 ± 0.04	−3.9 ± 0.2	3.1 ± 0.7
	3	−5.49 ± 0.10	−5.2 ± 0.6	1.1 ± 1.6
	4	−6.25 ± 0.15	−4.6 ± 0.9	5.5 ± 2.5
	5	−5.6 ± 0.2^{a}	...	...
	6	−5.5 ± 0.2^{a}	...	...
E → Z	7	−2.12 ± 0.03	−2.3 ± 0.2	−0.7 ± 0.5
	8	−2.83 ± 0.05	−2.9 ± 0.2	−0.3 ± 0.5
	9	−3.2 ± 0.2^{a}	...	...
	10	−1.04 ± 0.04	−0.2 ± 0.2	2.9 ± 0.6

^{a}Estimated errors.

RESULTS AND DISCUSSION

The results of the equilibration experiments are given in Table 1. Compounds **5**, **6** and **9** were readily decomposed during the equilibrations, especially at elevated temperatures (above room temperature), and the variation of the equilibrium constant with temperature could not be determined with adequate accuracy. Hence only the values of $\Delta G^{\ominus}$ at 298 K are given for these compounds. The Z,E forms of **1–6** are statistically favored by a factor of 2, and to eliminate this effect the values of $\Delta S^{\ominus}$ for the E,E→Z,E reactions should be decreased by 5.8 J K^{-1} mol^{-1} (=R ln 2) and those of $\Delta G^{\ominus}$ increased by 1.72 kJ mol^{-1} (= 298.15 R ln 2). For the Z,E→Z,Z reactions equal but opposite corrections should be made. No statistical corrections are necessary for the E,E→Z,Z reactions.

The values of $\Delta G^{\ominus}$ of the E,E→Z,Z (**1–6**) and E→Z (**7–9**) reactions decrease as the hydrogen atoms in the O–CH$_2$–O grouping are replaced by bulkier groups. On going from **1** to **5**, the decrement in $\Delta G^{\ominus}$ of the E,E→Z,Z reaction is about 1.5 kJ mol^{-1}. For comparison, when the hydrogen atoms of the methylene group in CH_3–CH_2–$OCH{=}CHCH_3$ are replaced with Me groups, the values of $\Delta G^{\ominus}$ of the E→Z reaction decrease by about 3.0 kJ mol^{-1},[1] and in the latter case there is only one Me group that undergoes the E→Z transfer. Hence the thermodynamics of the unsaturated acetals is considerably less sensitive to the bulkiness of the alkoxy group than that of alkyl propenyl ethers.

Trofimov *et al.*[2] have shown that in $ROCH{=}CH_2$ the C=C stretching frequency of the s-*cis* rotamer is found at about 1620 cm^{-1} and that of the other rotamer at about 1640 cm^{-1}. The relative intensity of the peak at about 1640 cm^{-1} increases with increasing bulkiness and increasing electron-withdrawing power of the R group. For R = n-$BuOCH_2$ the signal at about 1640 cm^{-1} is strong, i.e. the non-s-*cis* rotamer predominates. However, if R = n-$BuOCH_2CH_2$ the signal of the s-*cis* rotamer is strong. The same phenomenon is displayed in the results of this study. The value of $\Delta H^{\ominus}$ for 7E→7Z (R = $MeOCH_2$ in $ROCH{=}CHMe$) agrees with that for R = t-Bu,[1] which molecule probably exists in the s-*trans* (or near s-*trans*) configuration, whereas the value of $\Delta H^{\ominus}$ for R = $MeOCH_2CH_2$ **10** is in line with that (−0.65 ± 0.10 kJ mol^{-1}) for R = Et,[1] the E isomer of which probably exists mainly in the s-*cis* configuration.

Support for the predominance of the s-*trans* (s-*trans*, s-*trans*) rotamers in the unsaturated acetals **1–9** is obtained from NMR data. If the terminal hydrogen atoms of the vinyl group in $ROCH{=}CH_2$ are denoted by H_c and H_t (H *cis* to oxygen and H *trans* to oxygen, respectively), the difference (in ppm) in the chemical shifts, $\tau(H_t) - \tau(H_c)$, depends on R as follows:[3] 0.17 (R = Me), 0.16 (R = Et), 0.21 (R = i-Pr), 0.36 (R = t-Bu), 0.33 (R = $CH_2{=}CHOCH_2$). The increasing difference in the chemical shifts with increasing bulkiness of the alkyl group is undoubtedly a result of the decreasing s-*cis* rotamer content in the same sequence (in 2-methylenetetrahydrofuran, in which the "alkoxy" group necessarily exists in the s-*trans* configuration, the corresponding difference is 0.35 ppm[4]). For the compound $CH_2{=}CHOCH_2OCH{=}CH_2$, which can be regarded as the parent compound of **1–6**, the corresponding difference is slightly smaller than that for t-Bu vinyl ether, which cannot exist in the s-*cis* configuration due to steric factors.

Thus both the thermodynamic, IR and NMR data lead to the conclusion that the s-*trans* (s-*trans*, s-*trans*) rotamers should be considered as the most stable rotamers of all these unsaturated acetals.

EXPERIMENTAL

Preparation of **1**. A mixture of paraformaldehyde (15 g, 0.5 mol), allyl alcohol (60 g, 1 mol), hexane (70 ml) and p-toluenesulfonic acid (*ca* 1 g) were refluxed in a water-removal assembly until the evolution of water ceased. The mixture was made alkaline by NaOMe, and distilled to give 48 g (0.38 mol, 75%) of diallyl formal, b.p. 411 to 413 K at 101 kPa. A mixture of the formal (35 g), DMSO (50 ml) and t-BuOK (*ca* 2 g) was allowed to stand a few days at room temperature, after which the mixture was distilled to give a 71% yield of dipropenyl formal **1**, b.p. 319 to 321 K at 5.5 kPa. More than 90% of the isomer mixture obtained consisted of the Z,Z-isomer.

Preparation of **2**, **3**, b.ps 308 to 313 K at 0.9 to 1.0 kPa and 323 K at 0.9 kPa, prepared analogously to **1**. **4** was separated from the reaction mixture containing DMSO by extraction with hexane. The combined extracts were washed with water, dried ($CACl_2$), and distilled. A 50% yield of **4**, b.p. 339 K at 1.6 kPa, was obtained from pivalaldehyde diallyl acetal.

Preparation of **5**. An 80% yield of acetone diallyl acetal, b.p. 315–316 K at 1.3 kPa, was obtained from acetone, triallyl orthoformate and allyl alcohol.[5] The diallyl acetal was converted into **5** as described above for **4**. The yield was about 70%, and the product was collected at 327–329 K at 2.7 kPa.

Preparation of **6**. Cyclopentanone dimethyl acetal (b.p. 326 K at 4.0 kPa) was prepared in 59% yield from cyclopentanone and trimethyl orthoformate in methanol as in **5**. The product was converted into cyclopentanone diallyl acetal (b.p. 363–365 K at 1.9 kPa) by acid-catalyzed transacetalization. The diallyl acetal was then isomerized into **6** (b.p. 364–369 K at 2.4 kPa, yield 60%) as described for **4**.

Preparation of **7**. 6 g of formaldehyde methyl allyl acetal (b.p. 369–370 K at 101 kPa) was obtained from paraformaldehyde (20 g), methanol (20 g), and allyl alcohol (45 g), as described in connection with the preparation of **1**. Isomerization into **7** (b.p. 368–369 K at 101 kPa, yield 30%) was performed as described for **1**.

Preparation of **8**. Gaseous methyl vinyl ether was bubbled into allyl alcohol containing some p-toluenesulfonic acid until the alcohol had completely reacted with the vinyl ether (the reaction was followed by GLC). The reaction mixture was made alkaline with NaOMe, and distilled to give a 31% yield of acetaldehyde methyl allyl acetal, b.p. 387 K at 102 kPa. The product was isomerized into **8** (b.p. 383 K at 102 kPa, yield 50%) as described for **1**.

Preparation of **9**. Methyl isopropenyl ether (b.p. 313 K at 101.5 kPa) was prepared from acetone dimethyl acetal in 55% yield by fractionation of a mixture of the acetal (70 ml) and quinoline (100 ml) over a small amount of toluene p-sulfonic acid. A catalytic amount of the same acid was dissolved into allyl alcohol and an equimolar amount of the ether prepared above was slowly added to this solution with external cooling. The formation of acetone methyl allyl acetal was rapidly completed, and the product obtained was isomerized into **9** (b.p. 394 to 397 K at 102 kPa) as for **4**. The yield was 20%.

Preparation of **10**. Propionaldehyde 2-methoxyethyl acetal was prepared as described above for diallyl formal (see **1**). The yield of the product, b.p. 366 to 367 K at 1.2 kPa, was 73%. The acetal was fractionated from a small amount of toluene p-sulfonic acid to give a 30% yield of **10** (E:Z ≅ 1:1), b.p. 405–407 K at 101 kPa.

The ^1H NMR spectra of the compounds prepared were in agreement with the expected structures. For **1–9** the spectra of the propenyl groups in **2**(E,E) and **2**(Z,Z) are given here as typical examples of the positions of signals and values of coupling constants, which were practically insensitive to changes in R^1 and R^2 (60 MHz, CCl_4, τ values in ppm, coupling constants in Hz): **2**(E,E): 3.89 (H_α, J_{trans} 12.4, $J_{allylic}$ 1.2), 5.10 (H_β), 8.49 (Me-C=C, J_{vic} 5.4); **2**(Z,Z): 3.93 (H_α, J_{cis} 6.6, $J_{allylic}$ 1.7), 5.57 (H_β), 8.46 (Me-C=C, J_{vic} 5.4). For **10E**, the corresponding signals were found at 3.84 (H_α), 5.35 (H_β), 8.46 (Me); for **10Z** at 4.12 (H_α), 5.74 (H_β), 8.46 (Me).

Equilibrations. The equilibrations were conducted in the neat liquid with mercuric acetate as catalyst (see refs. 6 and 1). The position of equilibrium was approached from at least two starting mixtures of isomers. Since the synthetic products of **1–9** consisted of mainly the Z,Z (Z) isomer, the synthetic products were first equilibrated with $Hg(OAc)_2$ as catalyst, distilled, and then treated with preparative GLC (Carbowax 20 M column) to separate the other (Z,E; E,E, or E) isomers for starting materials for the equilibrations. The equilibrated samples were analyzed by GLC (Carbowax 20 M column, order of elution Z,Z; Z,E: E,E for **1–6**; Z; E for **7–10**). More details of the equilibration procedure are given in Ref. 1. In most cases the values of the equilibrium constant were determined at several temperatures between 271 (298) and 403 K.

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