

Short Communications

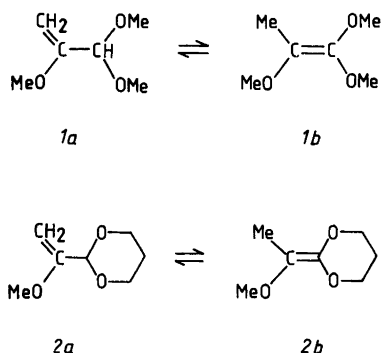
Thermodynamics of Vinyl Ethers. XXXII.* Thermodynamic Stability of Tri-alkoxy Substituted Derivatives of Ethylene

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It is well known that in mono-alkoxy substituted ethylenes ($\text{ROCH}=\text{CH}_2$) the alkoxy group has a strong stabilizing effect on the olefinic linkage (from the difference in the values of the enthalpies of hydrogenation of ethylene and ethyl vinyl ether, the stabilization energy of an EtO group is obtained as *ca.* 25 kJ mol^{-1}).¹ In poly-alkyl derivatives of ethylene the stabilization energies of alkyl groups appear to be roughly additive, if due allowance is made for steric interactions between the substituents.² However, in previous work³ the stabilizing effects of alkoxy groups have been found to be non-additive: the thermodynamic stability of a 1,2-di-alkoxy derivative of ethylene is comparable to that of an isomeric mono-alkoxy derivative. In other words, in $\text{ROCH}=\text{CHOR}$ the stabilization energies of the alkoxy groups are approximately halved, relative to their values in the respective mono-alkoxy derivatives of ethylene.

In the present work, the isomer equilibria $1a \rightleftharpoons 1b$ and $2a \rightleftharpoons 2b$ have been used to study the thermodynamic stability of a tri-alkoxy substituted derivative of ethylene, relative to that of an isomeric mono-alkoxy substituted one.



Experimental. Materials. 2,3,3-Trimethoxypropene (1a). Pyruvaldehyde dimethyl acetal was converted into 1,1,2,2-tetramethoxypropane by treatment of the acetal with $\text{HC}(\text{OMe})_3$ in MeOH with *p*-toluenesulfonic acid as a catalyst.⁴ The acetal formed was not isolated, however, but distillation of the reaction mixture was continued to effect the cleavage of the acetal into a mixture of MeOH and the desired vinyl ethers. Only pure 1a, b.p. $74^\circ\text{C}/55$ Torr, together with some uncleaved acetal, b.p. $84^\circ\text{C}/55$ Torr, was collected. No sign of the presence of 1b was detected.

2-(1-Methoxyvinyl)-1,3-dioxane (2a). 2-Acetyl-1,3-dioxane (b.p. $64^\circ\text{C}/9$ Torr) was prepared in 63 % yield by transacetalization of pyruvaldehyde dimethyl acetal with

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1,3-propanediol, using *p*-toluenesulfonic acid as a catalyst. This compound was then converted into the corresponding dimethyl acetal as described above for *1a*. Pure *2a* was collected at 78 °C/9 Torr (the acetal boiled at 84 °C/9 Torr). No sign of the presence of *2b* was found.

¹H NMR spectra (60 MHz, CCl₄, δ values). *1a*: 3.15 (2 MeO), 3.46 (MeO), 3.98 and 4.25 (d, *J* 2 Hz, olefinic protons), 4.48 (CH). *2a*: 1.1–2.4 (m, 2H), 3.45 (MeO), 3.6–4.2 (m, 4H), 3.90 and 4.25 (d, *J* 2 Hz, olefinic protons), 4.62 (CH).

¹³C NMR spectra (15 MHz, CDCl₃, δ values in ppm from internal TMS). *1a*: 83.8 (C-1), 158.5 (C-2), 101.5 (C-3), 53.2 (2 MeO), 55.0 (MeO). *2a*: 83.3 (=CH₂), 159.3 (C=CH₂), 99.6 (CH), 67.3 (2 CH₂), 25.6 (CH₂), 55.1 (MeO).

Equilibration experiments. The equilibrations were carried out in an inert solvent (benzene, CCl₄) with I₂ as a catalyst, as amply illustrated in the previous parts of this series. Thus, ca. 20 % (v/v) solutions of the synthetic products in the solvent selected (ca. 0.01 M in I₂) were enclosed in glass ampoules, which were thermostatted at temperatures from 100 to 170 °C, and the progress of isomerization was monitored by analysis of the reaction mixture by GLC and ¹H NMR spectroscopy. However, no signs of the formation of the *b* isomers could be detected in spite of extended reaction times (usually, the equilibrium state is achieved within a few minutes or hours at the high temperatures used; in this case the reactions were followed for several weeks).

Results and discussion. As stated above, the attempts to detect the presence of the *b* isomers in the equilibrium mixtures failed, suggesting very low thermodynamic stabilities for these compounds. In agreement with this observation is the fact that no signs of the *b* forms were found in the synthetic mixtures (at the high temperatures used in the cleavage of the acetals into vinyl ethers, the formation of the thermodynamically less stable isomers should be particularly favored). The conclusion to be drawn from these findings is obvious: the presence of three alkoxy groups at a C=C linkage gives rise to a strongly destabilized system, relative to an isomeric mono-alkoxy derivative of ethylene. Since it is likely that the presence of the *b* isomers could have been detected had their concentration been 1 % or more of that of the *a* forms, it follows that the equilibrium constant *K*(*b/a*) is less than 0.01 at the temperatures employed (100–170 °C); hence the value of Δ*G*[⊖] for the *a*→*b* reaction must be higher than +14 kJ mol⁻¹ under these conditions.

In summary, a single alkoxy group bound to a C=C bond has a strong stabilizing effect on the bond; the presence of two alkoxy groups at adjacent olefinic atoms gives rise to no additional stability, whereas three alkoxy groups at a C=C bond bring about a strongly destabilized system.

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