

Thermodynamics of Vinyl Ethers. XXIX.* Relative Stabilities of Isomeric Methoxy-Substituted Octalins

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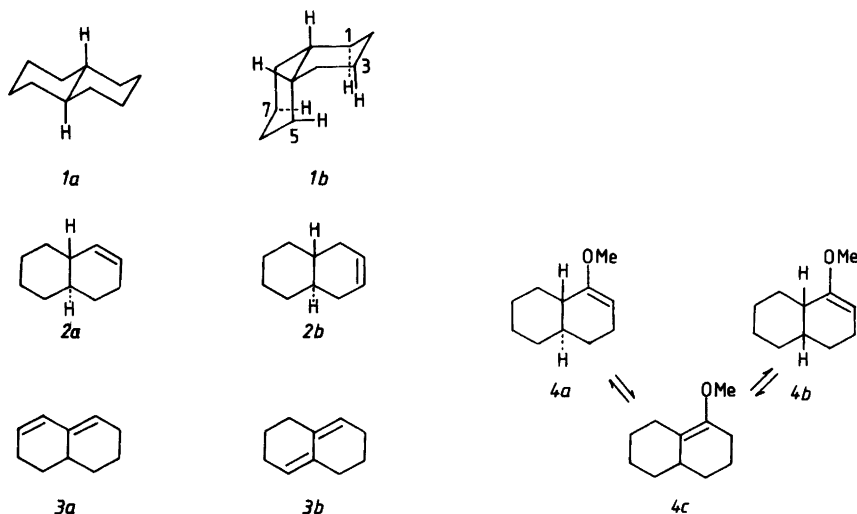
The relative thermodynamical as well as thermochemical stabilities of the *cis* and *trans* forms of 8-MeO-1,2,3,4,4a,5,6,8a-octahydronaphthalene and 8-MeO-1,2,3,4,4a,5,6,7-octahydronaphthalene have been determined by chemical equilibration in cyclohexane solution at various temperatures. The *trans* compound is shown to be the most stable isomeric species, the value of ΔH^\ominus for the *trans*→*cis* isomerization being $1.9 \pm 0.2 \text{ kJ mol}^{-1}$, to be compared with an enthalpy difference of *ca.* 11 kJ mol^{-1} between the respective forms of the corresponding saturated carbocycle, decahydronaphthalene (decalin).

Thermochemical studies on the isomeric forms of decalin (decahydronaphthalene) have shown that the *trans* form (*1a*) has the higher thermochemical stability, the enthalpy difference ΔH^\ominus between the *cis* and *trans* forms being 11 kJ mol^{-1} in the liquid phase and 13 kJ mol^{-1} in the gaseous phase.^{1,2} Other related studies in this field include an equilibration investigation on the relative stabilities of the *trans* octalins *2a* and *2b*, as well as on those of the corresponding *cis* isomers.³ Of considerable interest is also the work of Bates *et. al.*⁴ on the relative stabilities of some isomeric hexahydronaphthalenes, such as *3a* and *3b*. In the present paper, the results of an equilibration study on the methoxy-substituted octalins *4a*–*4c* are described. As moderately reactive vinyl ethers, these compounds are readily interconvertible by iodine in an inert solvent (cyclohexane) and thus the thermodynamical equilibrium is easily established under mild conditions, without significant side reactions. Of particular interest was the equilibrium between the *trans* and *cis* forms *4a* and *4b*.

RESULTS AND DISCUSSION

The compositions of the equilibrium mixtures at various temperatures are shown in Table 1 and the values of the thermodynamic functions ΔG^\ominus , ΔH^\ominus and ΔS^\ominus of isomerization at 298.15 K in Table 2. The *trans* form *4a* is shown to be the thermodynamically (as well as the thermochemically) most stable isomer. The entropy difference between the *cis* and *trans* forms is negligible ($0.5 \pm 0.6 \text{ J K}^{-1} \text{ mol}^{-1}$) whereas the enthalpy of the *cis* form is *ca.* 1.9 kJ mol^{-1} higher than that of the *trans* isomer, to be compared with the enthalpy difference of *ca.* 11 kJ mol^{-1} between *cis* and *trans*-decalins in the liquid phase.¹ The observed enthalpy difference between *4a* and *4b* is reasonable in view of the structural changes involved on

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going from the saturated carbocycles *1a* and *1b* to the present unsaturated compounds *4a* and *4b*: on replacement of the C_1-C_2 single bond of *1b* by a $C=C$ bond, the destabilizing gauche interactions $C_1\cdots C_5$ and $C_1\cdots C_7$ are completely lost and the gauche interaction between the axial $C-H$ bonds at C_3 and C_5 is altered to an apparently less destabilizing gauche interaction between the axial $C-H$ bond at C_5 and the pseudoaxial $C-H$ bond at C_3 .⁵ Ascribing an energy contribution of 3.3 kJ mol^{-1} to each gauche interaction², the difference of *ca.* 9 kJ mol^{-1} between the relative thermochemical stabilities of the *cis* and *trans* forms of *1* and *4* is easily understood.

The configurations of the geometrical isomers *4a* and *4b* were assigned on the basis of some differences in their ^{13}C NMR spectra. It is well known that the C atoms at the ring

Table 1. Compositions of the equilibrium mixtures at various temperatures.

<i>T</i> /K	<i>c</i> (<i>4a</i>)/%	<i>c</i> (<i>4b</i>)/%	<i>c</i> (<i>4c</i>)/%
298	52.9	25.8	21.3
333	51.2	27.2	21.6
363	47.0	26.6	26.4
393	46.4	27.0	26.6
423	43.6	26.9	29.5

Table 2. Values of the thermodynamic parameters ΔG^\ominus , ΔH^\ominus and ΔS^\ominus at 298.15 K (cyclohexane solution). The errors are twice the standard errors.

Reaction	$\Delta G^\ominus/\text{kJ mol}^{-1}$	$\Delta H^\ominus/\text{kJ mol}^{-1}$	$\Delta S^\ominus/\text{J K}^{-1} \text{ mol}^{-1}$
<i>4a</i> → <i>4b</i>	1.77(0.05)	1.91(0.22)	0.5(0.6)
<i>4a</i> → <i>4c</i>	2.39(0.34)	4.6(1.6)	7(4)
<i>4b</i> → <i>4c</i>	0.62(0.32)	2.7(1.5)	7(4)

junctions of *1a* and *1b* absorb at markedly different frequencies, namely, at 37.6 (*cis*) and 44.9 (*trans*) ppm.⁶ In the present compounds, the non-equivalent ring junction carbon atoms of the thermodynamically less stable isomer absorbed at 39.9 and 34.2 ppm and those of the other geometrical isomer at 44.6 and 41.4 ppm. Thus it is obvious that the former compound has the *cis* configuration and the latter isomer the *trans* configuration. This configurational assignment is in agreement with their relative stabilities as explained above.

EXPERIMENTAL

Materials. A roughly equimolar mixture of *4a*, *4b* and *4c* was obtained by treatment of 1-decalone with trimethyl orthoformate in methanol with *p*-toluenesulfonic acid as catalyst.⁷ The yield of the product, b.p. 80–82 °C at 3 Torr, was 70 %. The mixture was further fractionated using a Perkin-Elmer M 251 Auto Annular Still to get the following mixtures of isomers, which were used for recording the spectra and for the equilibration experiments: (A) *4a* (31.3 %), *4b* (5.7 %), *4c* (62.9 %); (B) *4a* (40.8 %), *4b* (42.8 %), *4c* (16.4 %).

¹H NMR spectra (60 MHz, CCl₄, δ values in ppm from TMS, coupling constants in Hz). *4a*: 0.9–2.3 (ring hydrogens), 3.35 (MeO), 4.35 (olefinic proton, *J* 4); *4b*: 0.9–2.3 (ring hydrogens), 3.37 (MeO), 4.37 (olefinic proton, *J* 4); *4c*: 0.7–2.2 (ring hydrogens), 3.36 (MeO).

¹³C NMR spectra (15 MHz, CDCl₃, δ values in ppm from TMS). Since the spectra were recorded on mixtures of isomers, not on pure compounds, signal assignment of the very similar saturated carbon atoms of the cyclic skeleton proved to be difficult. Hence only signals which could be assigned with certainty (CH₃OC_α=C_β, ring junction C atoms) are given here. *4a*: 41.4, 44.6 (ring junction C atoms), 53.9 (MeO), 92.4 (C_β), 157.2 (C_α); *4b*: 34.2, 39.3 (ring junction C atoms), 53.9 (MeO), 91.3 (C_β), 159.1 (C_α); *4c*: 37.1 (ring junction C atom), 53.6 (MeO), 121.1 (C_β), 146.5 (C_α).

Equilibrations. Cyclohexane was used as solvent and iodine as catalyst. The position of equilibrium was approached from two different mixtures of isomers (see *Materials*). The values of Δ*G*[⊖], and Δ*H*[⊖] and Δ*S*[⊖] at 298.15 K were obtained by linear least-square treatment of ln *K* vs. *T*⁻¹. For other details see Ref. 8.

REFERENCES

1. Cox, J.D. and Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic, London and New York 1970.
2. Mortimer, C.T. *Reaction Heats and Bond Strengths*, Pergamon, Frankfurt am Main 1962, p. 30.
3. Oberhänsli, P. and Whiting, M.C. *J. Chem. Soc. B* (1969) 467.
4. Bates, R.B., Carnighan, R.H. and Staples, C.E. *J. Am. Chem. Soc.* 85 (1963) 3030.
5. Kagan, H.B. *Organische Stereochemie*, Thieme, Stuttgart 1977, p. 55.
6. Stothers, J.B. *Carbon-13 NMR Spectroscopy*, Academic, New York and London 1972, p. 63.
7. House, H.O. and Kramar, V. *J. Org. Chem.* 28 (1963) 3362.
8. Taskinen, E. *J. Chem. Thermodyn.* 5 (1973) 783.

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