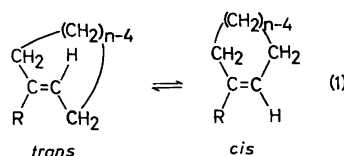


Thermodynamics of Vinyl Ethers. XXVI.* Relative Stabilities of the Geometrical Isomers of 8- to 15-Membered 1-Methoxycycloalkenes

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The relative stabilities of the *cis* and *trans* forms of 8- to 15-membered 1-methoxycycloalkenes (excluding 1-methoxycyclotetradecene) have been determined by chemical equilibration in cyclohexane solution at several temperatures. In each case the *cis* isomer is the thermodynamically more stable species at 298.15 K. In the 8- and 9-membered rings, the equilibrium concentration of the *trans* form was so low that the peak corresponding to this isomer could not be detected by GLC analysis of the equilibrium mixture. For the *trans*→*cis* isomerization of 1-methoxycyclododecene $\Delta G^\ominus = -16.7 \text{ kJ mol}^{-1}$ at 298.15 K and on going to larger ring sizes the value of ΔG^\ominus increases by 10 kJ mol^{-1} or more, so that for 1-methoxycyclopentadecene the *trans*→*cis* reaction has $\Delta G^\ominus = -3.8 \text{ kJ mol}^{-1}$. The reaction enthalpies and entropies reveal the same surprising variations with ring size that have previously been observed for the corresponding cycloalkenes.

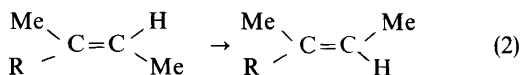


in reaction 1) is a slightly endothermic but the reaction *trans*-cyclododecene→*cis*-cyclododecene ($n=12$, $R=H$) slightly exothermic. The reaction entropies were also surprisingly irregular, cf. $\Delta S^\ominus = +13 \text{ J K}^{-1} \text{ mol}^{-1}$ for $n=9$ while $\Delta S^\ominus = -19 \text{ J K}^{-1} \text{ mol}^{-1}$ for $n=10$ ($R=H$).

In the present paper, the results of an equilibrium study of reaction 1 with $R=MeO$ are described. The work stems from our interest in the thermodynamics of alkoxy-substituted olefins (vinyl ethers). Particularly, the work aimed at possible detection of the same “anomalies” in the thermodynamics of reaction 1 for $R=MeO$ which have previously been found for the case $R=H$. For that purpose, 8- to 15-membered 1-methoxycycloalkenes were prepared and the thermodynamics of their *trans*-*cis* isomerization were studied by I_2 catalyzed equilibration in cyclohexane solution.

RESULTS AND DISCUSSION

The results of the equilibration experiments are shown in Tables 1 and 2. Prior to consideration of the thermodynamic data, it is advantageous to evaluate the effect of replacing an olefinic hydrogen in acyclic alkenes by a MeO group on the



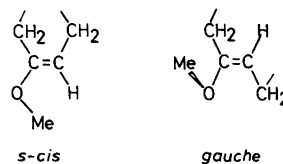
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Table 1. Values of the mean equilibrium constant $K(\text{cis}/\text{trans})$ for some 1-methoxycycloalkenes in cyclohexane solution at various temperatures.

Ring size (n)	K (temperature in K)
10	157 (373), 107 (393), 78.3 (413), 62.5 (433), 46.9 (453)
11	12.9 (298), 8.88 (333), 7.36 (353), 5.08 (403), 4.28 (433)
12	14.2 (298), 9.56 (333), 7.95 (353), 5.74 (393), 4.72 (423), 3.82 (453)
13	6.66 (298), 4.86 (333), 3.37 (393), 2.46 (453)
15	4.71 (298), 3.96 (333), 3.73 (363), 3.65 (393), 3.35 (423), 3.15 (453)

thermodynamics of *trans-cis* isomerization. This may be accomplished by means of reaction 2. When $R=H$, $\Delta G^\ominus(\text{g}) = +2.85 \text{ kJ mol}^{-1}$, $\Delta H^\ominus(\text{g}) = +4.2 \text{ kJ mol}^{-1}$ and $\Delta S^\ominus(\text{g}) = +4.2 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298.15 K (Ref. 3) and when $R=MeO$, $\Delta G^\ominus = -6.10 \text{ kJ mol}^{-1}$, $\Delta H^\ominus = -10.3 \text{ kJ mol}^{-1}$ and $\Delta S^\ominus = -13.9 \text{ J K}^{-1} \text{ mol}^{-1}$ (cyclohexane solution⁴). Thus the MeO substitution decreases the value of ΔG^\ominus by 9 kJ mol^{-1} , that of ΔH^\ominus by 15 kJ mol^{-1} and that of ΔS^\ominus by $18 \text{ J K}^{-1} \text{ mol}^{-1}$. Comparison of the ΔG^\ominus data given in Table 2 for the cyclic olefins and the corresponding vinyl ethers shows that in the 10-, 11- and 12-membered cyclic compounds the effect of a 1-MeO substituent on ΔG^\ominus does not substantially differ from that found in acyclic alkenes because the MeO group induced decrements in ΔG^\ominus are 7.4, 8.8 and 7.9 kJ mol^{-1} ,

respectively. On the other hand, in the cyclic compounds the MeO substitution has a markedly smaller effect on the values of the reaction enthalpy (the decrements in ΔH^\ominus are 6, 9 and 8 kJ mol^{-1} in the 10-, 11- and 12-membered compounds, respectively) than in the acyclic compounds. The same applies to the effect of the MeO substitution on the ΔS^\ominus values (the respective decrements in ΔS^\ominus are 5, 2 and $0 \text{ J K}^{-1} \text{ mol}^{-1}$). The enthalpy data thus suggest that either (a) the act of replacing an olefinic hydrogen in the product of reaction 1 by a MeO group has a more positive effect on the enthalpy content of the parent olefin than a similar substitution brings about on that of the product of reaction 2 or (b) the act of replacing an olefinic hydrogen in the reactant of reaction 1 by a MeO group has a more negative effect on the enthalpy content of the parent olefin than a similar substitution brings about on that of reaction 2. It is difficult to give any reasonable explanation supporting alternative (a) since both in the cyclic and acyclic compounds the MeO group apparently has equal chances to assume the energetically favorable *s-cis* conformation. On the other hand, in



the reactants the MeO group is forced to adopt the high-energy nonplanar *gauche* conformation⁵ and

Table 2. Values of ΔG^\ominus , ΔH^\ominus and ΔS^\ominus at 298.15 K for the *trans*→*cis* isomerization of some cycloalkenes ($R=H$) and the corresponding 1-methoxycycloalkenes ($R=MeO$). Solvents: Acetic acid ($R=H$) and cyclohexane ($R=MeO$). The errors are twice the standard errors.

Ring size (n)	$\Delta G^\ominus/\text{kJ mol}^{-1}$		$\Delta H^\ominus/\text{kJ mol}^{-1}$		$\Delta S^\ominus/\text{J K}^{-1} \text{ mol}^{-1}$	
	$R=H^a$	$R=MeO$	$R=H^a$	$R=MeO$	$R=H^a$	$R=MeO$
8			-38.4^b			
9	$-16.0(0.3)$		$-12.1(1.4)$		13(3)	
10	$-9.22(0.06)$	$-16.7(0.4)$	$-14.9(0.3)$	$-20.8(1.2)$	$-19.2(0.7)$	$-14(3)$
11	$2.34(0.01)$	$-6.33(0.03)$	$0.5(0.1)$	$-8.8(0.1)$	$-6.1(0.1)$	$-8.2(0.3)$
12	$1.29(0.01)$	$-6.60(0.07)$	$-1.7(0.1)$	$-9.5(0.3)$	$-10.0(0.1)$	$-9.6(0.7)$
13		$-4.70(0.08)$		$-7.2(0.3)$		$-8.3(0.8)$
15		$-3.78(0.12)$		$-2.7(0.5)$		$3.7(1.3)$

^a Calculated from the equilibrium data given in Ref. 2. ^b From heats of hydrogenation (Ref. 1).

Table 3. ^1H NMR^a and ^{13}C NMR^b spectroscopic data for some characteristic signals of 8- to 15-membered 1-methoxycycloalkenes.

Ring size (n)	^1H NMR						^{13}C NMR					
	$\delta(\text{MeO})$		$\delta(=\text{CH})$		J_{vic}/Hz		$\delta(\text{C-1})$		$\delta(\text{C-2})$		$\delta(\text{MeO})$	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
8	3.36		4.31		8.0		158.48		94.42		53.99	
9	3.38		4.32		8.3		158.19		96.20		53.99	
10	3.40		4.19		8.0		156.02		97.17	110.44	53.88	
11	3.43	3.47	4.16	4.55	7.5	7.5	156.08		98.83	112.21	53.88	56.10
12	3.38	3.43	4.18	4.48	7.6	7.5	156.59	154.13	97.97	112.90	53.88	56.28
13	3.35	3.38	4.12	4.38	7.0	7.0	156.77	154.65	97.63	112.27	53.93	56.22
15	3.36	3.40	4.18	4.37	7.0	6.8	157.10	154.65	96.83	111.18	53.88	56.16

^aIn CCl_4 . ^bIn CDCl_3 .

alternative (b) suggests that in the reactant of reaction 1 the MeO group can assume a less strained (less nonplanar) *gauche* structure than in that of reaction 2. In this case p - π conjugation should be more efficient in the $\text{O}=\text{C}=\text{C}$ system of the cyclic reactants than in that of the acyclic reactant and thus the difference in the ^{13}C NMR chemical shift values of C-2 between the geometrical isomers of the cyclic compounds should be smaller than the corresponding difference for the respective C atom (C-3) in the acyclic compounds of reaction 2 ($\text{R}=\text{MeO}$).⁵ However, the experimental results do not support this view: For the 10-, 11-, 12-, 13- and 15-membered cyclic compounds ($\text{R}=\text{MeO}$) the values of the difference $\delta(\text{C-2})_{\text{trans}} - \delta(\text{C-2})_{\text{cis}}$ (Table 3) amount to 13.3, 13.4, 14.5, 14.6 and 14.4 ppm, respectively, while the corresponding difference for the acyclic compounds is 12.5 ppm.⁵

On average, the values of $\Delta G^\ominus(298.15\text{ K})$ of reaction 1 are *ca.* 8.0 kJ mol^{-1} more negative for $\text{R}=\text{MeO}$ than for $\text{R}=\text{H}$ ($n=10-12$). Thus it may be expected that for the *trans*→*cis* isomerization of 1-methoxycyclononene ($n=9$), the value of $\Delta G^\ominus(298.15\text{ K})$ is about $(-16.0-8.0)\text{ kJ mol}^{-1} = -24.0\text{ kJ mol}^{-1}$. This corresponds to an equilibrium constant $K(\text{cis/trans})$ of about 16000 at 298 K, which explains the fact that the peak of the *trans* isomer could not be detected in the gas chromatogram. The same explanation holds for 1-methoxycyclooctene.

EXPERIMENTAL

Materials. The 1-methoxycycloalkenes studied were prepared in 50–88% yields from the

corresponding cycloalkanones and trimethyl orthoformate in methanol with *p*-toluenesulfonic acid as catalyst.⁶ Physical constants: 1-Methoxycyclooctene b.p. 351–353 K at 1.5 kPa (pure *cis*), 1-methoxycyclononene b.p. 357–359 K at 1.3 kPa (pure *cis*), 1-methoxycyclodecene b.p. 369–375 K at 1.3 kPa (*cis/trans* ≈ 30), 1-methoxycycloundecene b.p. 383–386 K at 1.3 kPa (*cis/trans* ≈ 3), 1-methoxycyclododecene b.p. 401–402 K at 1.3 kPa (*cis/trans* ≈ 3), 1-methoxycyclotridecene b.p. 419–421 K at 1.6 kPa (*cis/trans* ≈ 2), 1-methoxycyclopentadecene b.p. 446–448 K at 1.6 kPa (*cis/trans* ≈ 2). As pure compounds or mixtures of isomers with sufficiently different compositions were needed for the spectral characterization and equilibrations, the crude reaction products were fractionally distilled. Some characteristic features of the ^1H NMR and ^{13}C NMR spectra of the compounds studied are shown in Table 3.

Equilibrations. The equilibration experiments were carried out in cyclohexane solution with I_2 as catalyst (the substrate and catalyst concentrations were *ca.* 1 M and 0.004 M, respectively).⁷ The equilibrated samples were analyzed by GLC using a Carbowax 20 M column, through which the compounds were eluted in the order *trans*, *cis*. The values of the equilibrium constant K at various temperatures are shown in Table 1. The values of ΔG^\ominus , ΔH^\ominus and ΔS^\ominus at 298.15 K (Table 2) were obtained by linear least-squares treatment of $\ln K$ against T^{-1} .

REFERENCES

- Turner, R. B. and Meador, W. R. *J. Am. Chem. Soc.* 79 (1957) 4133.
- Cope, A. C., Moore, P. T. and Moore, W. R. a. *J. Am. Chem. Soc.* 81 (1959) 3153; b. *J. Am. Chem. Soc.* 82 (1960) 1744.

3. Meyer, E. F. and Stroz, D. G. *J. Am. Chem. Soc.*, 94 (1972) 6344.
4. Taskinen, E. *J. Chem. Thermodyn.* 6 (1974) 345.
5. Taskinen, E. *Tetrahedron* 34 (1978) 425.
6. House, H. O. and Kramar, V. *J. Org. Chem.* 28 (1963) 3362.
7. Taskinen, E. *J. Chem. Thermodyn.* 5 (1973) 783.

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