

Relative Rate of Acid-catalysed Addition of Methanol to *cis*- and *trans*-Cyclo-octenes

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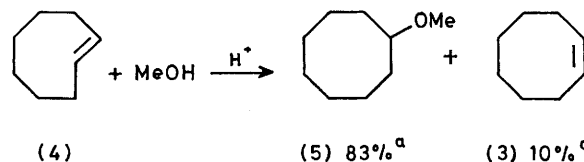
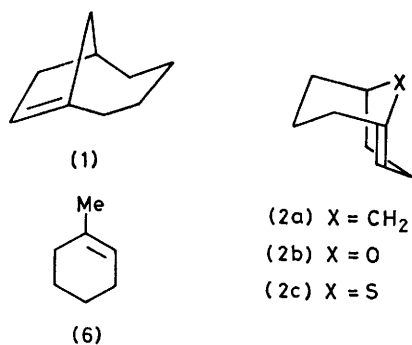
The relative rates of protonation of *cis*- and *trans*-cyclo-octenes were determined to be 1:3 000 in the acid-catalysed addition of methanol; this result is compared with those for related bridgehead alkenes in order to correlate the enhanced reactivities with their strain energies.

It has recently been shown that highly strained bridgehead alkenes such as bicyclo[4.2.1]non-1(8)-ene (**1**) and bicyclo[3.3.1]non-1-enes (**2**) undergo acid-catalysed hydration at anomalously rapid rates compared with suitable reference alkenes.¹ These bridgehead alkenes are related to *trans*-cyclo-octene and their high reactivities towards protons have been attributed to their strain energy (*ca.* 96 kJ mol⁻¹)² which arises mainly from the *trans*-cyclo-octene skeleton. The parent *trans*-cyclo-octene also possesses a strain energy of 70 kJ mol⁻¹, which is greater by 39 kJ mol⁻¹ than that for the *cis*-

isomer,² and therefore a much enhanced rate of protonation is expected. The hydration of *trans*-cyclo-octene has been examined at 52.4 °C in order to prove that the acid catalysis was general.³ No corresponding experiment on the *cis*-isomer was carried out.

We now report some aspects of the chemistry and kinetics of the acid-catalysed addition of methanol to *cis*- and *trans*-cyclo-octenes.

Addition experiments on the *cis*- and *trans*-cyclo-octenes⁴ (**3**) and (**4**) were run at 25.0 ± 0.1 °C in methanol containing sulphuric acid. The major product was, as expected, the addition product, methoxycyclo-octane (**5**),[†] although a small



Scheme 1. ^a Yields based on consumed (**4**).

[†] The authentic methoxycyclo-octane (**5**) was prepared by the reaction of cyclo-octanol with sodium hydride followed by methyl iodide.

Table 1. Rate (k_{obs}) of methanol addition catalysed by sulphuric acid in methanol at 25 °C.

Alkene (0.01 M)	H ₂ SO ₄ /M	$k_{\text{obs}}/\text{s}^{-1}$
<i>cis</i> -Cyclo-octene (3) ^a	1.0	$(1.7 \pm 0.9) \times 10^{-8}$
<i>trans</i> -Cyclo-octene (4)	0.03	$(1.42 \pm 0.03) \times 10^{-6}$
	1.0	$(5.06 \pm 0.13) \times 10^{-5}$

^aUnder the same conditions, *cis*-cycloheptene gave $k_{\text{obs}} = (2.2 \pm 0.3) \times 10^{-8} \text{ s}^{-1}$.

Table 2. Relative rate (k_{rel}) of acid-catalysed addition.

Alkene	S.E. ^a	k_{rel}
<i>cis</i> -Cyclo-octene (3) ^{b,c}	31	$\equiv 1.0$
<i>trans</i> -Cyclo-octene (4) ^{b,c}	70	3.0×10^3
1-Methylcyclohexene (6) ^{d,e}	7	$\equiv 1.0$
Bicyclo[4.2.1]nonene (1) ^{e,f}	—	9.1×10^2
Bicyclo[3.3.1]nonene (2a) ^{e,f}	96	1.03×10^5

^a Strain energy in kJ mol⁻¹; reference 2. ^b This work. ^c Measured in methanol solution. ^d W. K. Chwang, V. J. Nowlan, and T. T. Tidwell, *J. Am. Chem. Soc.*, 1977, **99**, 7233. ^e Measured in aqueous solution. ^f Ref. 1a.

amount of the *cis*-isomer (3) was also obtained (Scheme 1) in the reaction with (4), suggesting the intervention of a cyclo-octyl cation.

Disappearance of the substrate was monitored by g.l.c. analysis, using a β, β' -oxydipropionitrile column, of aliquots

removed from the reaction mixture and neutralized with an excess of potassium carbonate. Plots of the logarithm of the substrate concentration *versus* the reaction period gave good straight lines for all runs. The observed rate constants at different acidities are listed in Table 1. The relative rates (k_{rel}) derived from the above data are shown in Table 2 together with those obtained from the hydration of the bridge-head alkenes (1), (2a), and 1-methylcyclohexene (6) (to provide reference trisubstituted alkene). It is interesting to note that, provided that strain of the molecule is induced through the introduction of a double bond as is the case here, the rates of addition correlate well with the strain energies of the alkenes in spite of the different medium used.

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