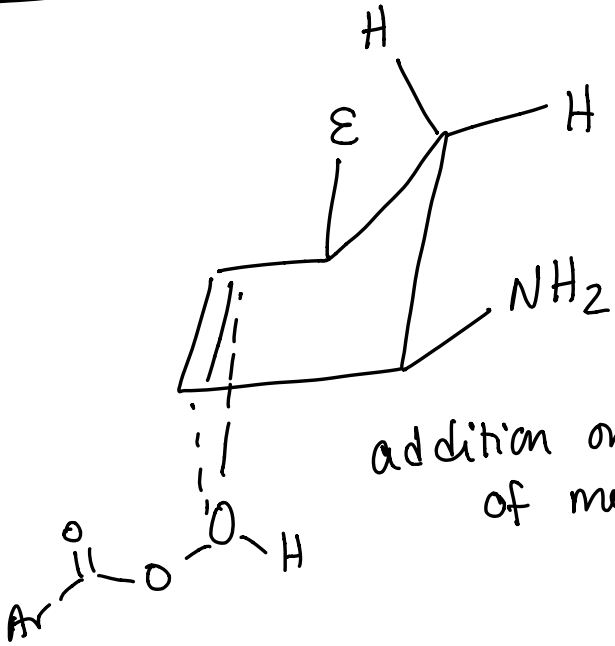
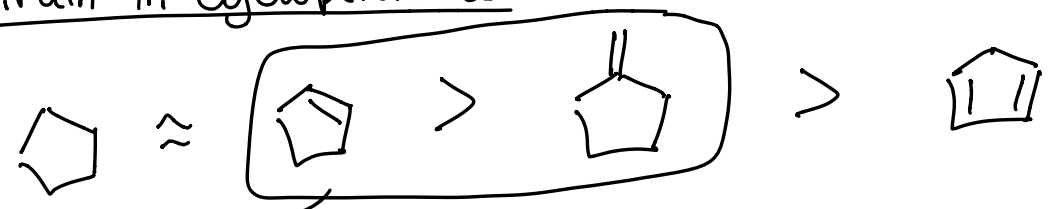
Lecture 10: Conformational Analysis of Cyclic Systems



addition on convex face of molecule.

Strain in cyclopentenes



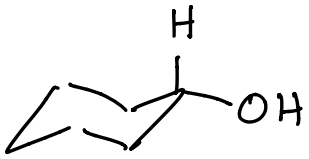
less eclipsing strain
outweighs increase in angle strain

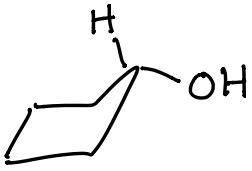
Cyclopentane derivatives → prefer sp^2 center in ring to minimize eclipsing interactions.

Rxns proceed to favor exo double bond.

In 6-membered ring: rxns proceed to avoid exo double bond.

ex

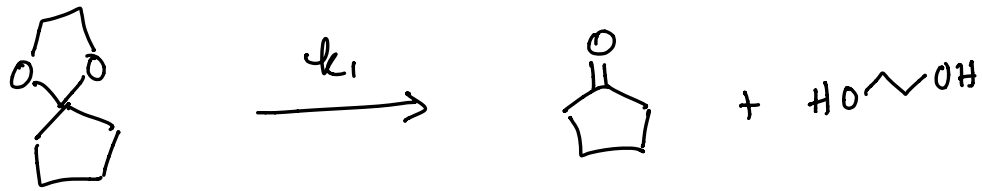


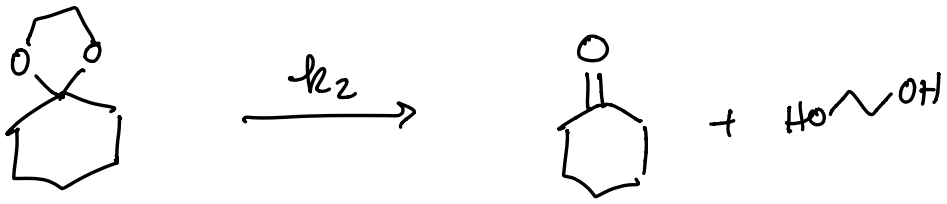


$$\frac{k_1}{k_2} = 23$$

Tetrahedron 1957, 221.

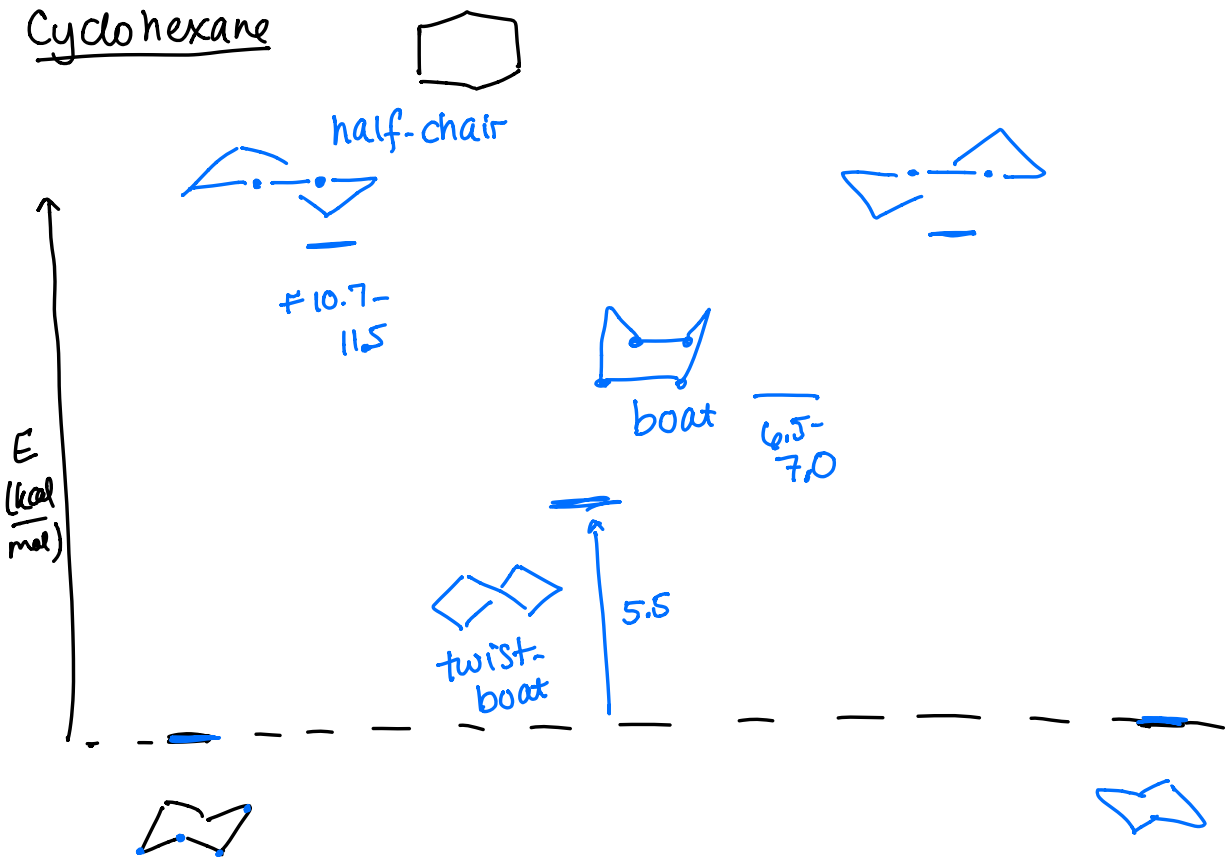
ex:





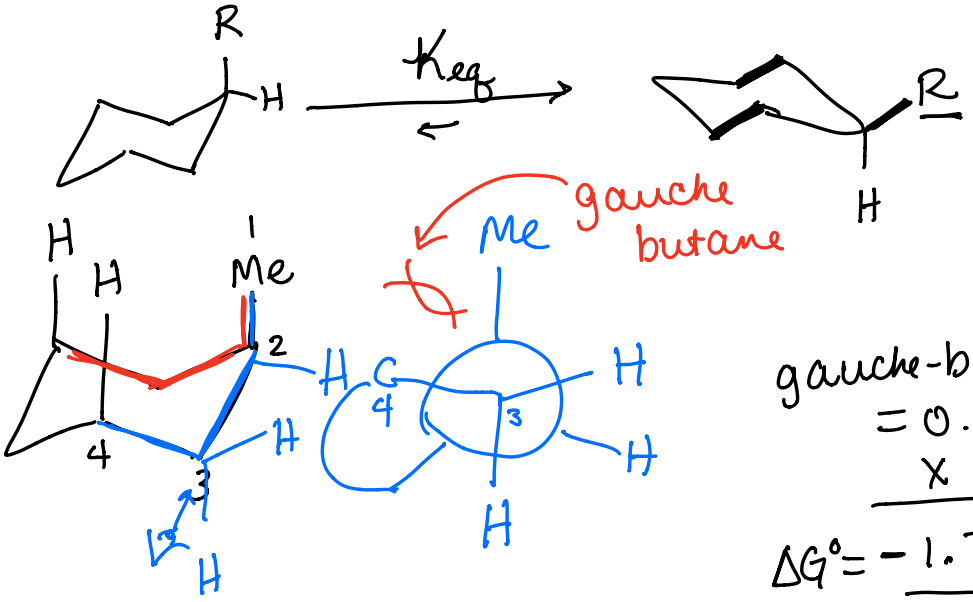
$$\frac{k_1}{k_2} = 13$$

Bull Soc Chim Fr 1976, 1935.


Cyclohexane
half-chair
≠ 10.7-11.5
boat
6.5-7.0
E (kcal/mol)
5.5
twist-boat

Substituent Effects

Monosubstituted:



gauche-butane
= 0.8
x 2
$\Delta G^\circ = -1.76 \text{ kcal/mol}$

A-value = 1.74

A-values

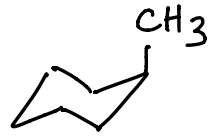
$$\Delta G^\circ = -RT \ln K_{eq}$$

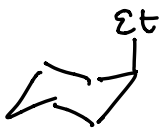
$$\text{A-value} = -\Delta G^\circ$$

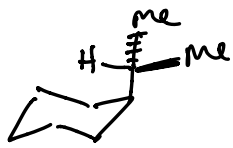
↳ preference of substituent to be in equatorial position.

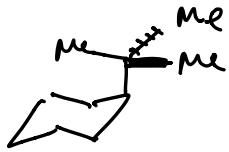
Table 2.14 in A & D.

A-values ∝ relative size (sometimes)

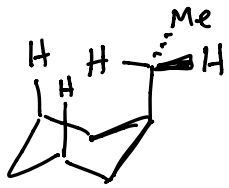


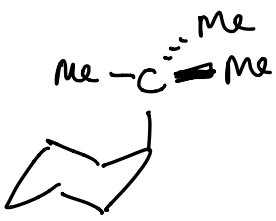


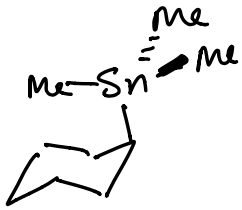




A-value 1.74 1.80 2.15 5.0







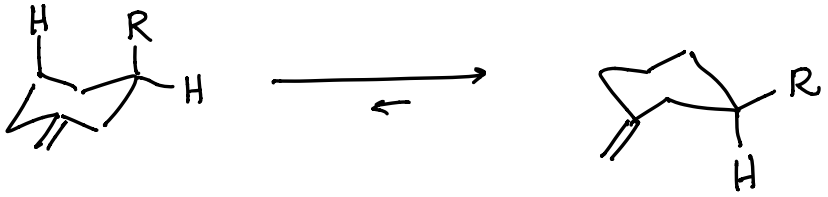
A-value 5.0 2.5 1.1

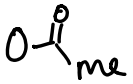
Covalent Radius C < Si < Sn

Bond Lengths: C–C < C–Si < C–Sn

So smaller effect although substituent is bigger.

Impact of Double Bonds



R	$-\Delta G^\circ$	A-value	
Me	0.8	1.74	Only 1 1,3-diaxial.
OMe	0.8	0.6	} Electrostatic effect of sp^2 C offsets reduced steric clash.
	0.6	0.71	

Disubstituted

If no interaction between substituents, A-values are roughly additive.

1,4:

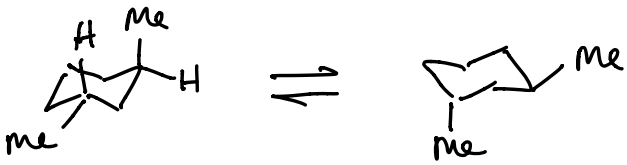
$\Delta G^\circ = 0$ kcal/mol

$\Delta G^\circ = -2(1.74$ kcal/mol$)$

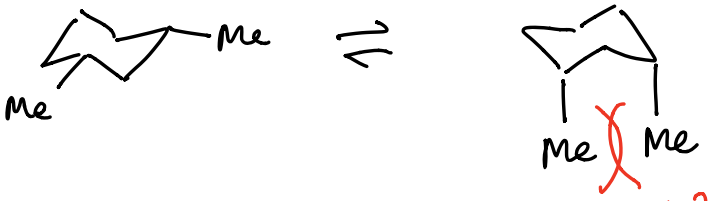
$\Delta G^\circ = -3.48$ kcal/mol

1,3: Additive only if trans

trans



cis



1,3 diaxial (syn-pentane)

$\Delta G^\circ = +5.5$ kcal/mol