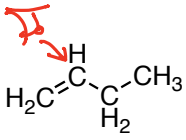
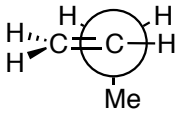
Lecture 9: Conformational Analysis

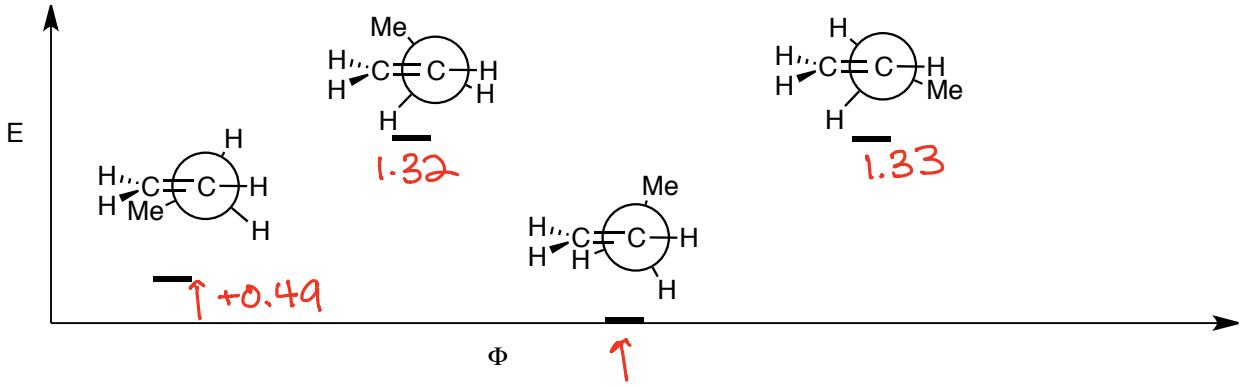
Announcements:
- Meet here on Thurs (not computer lab)
- Midterm 1 on Thurs, 10/6 (next week)

Today:
- Conformational analysis of acyclic systems
- Conformational analysis of cyclic systems

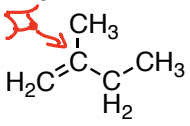
Butene

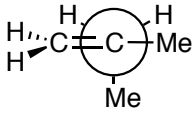


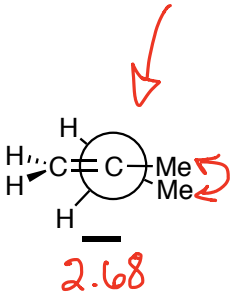


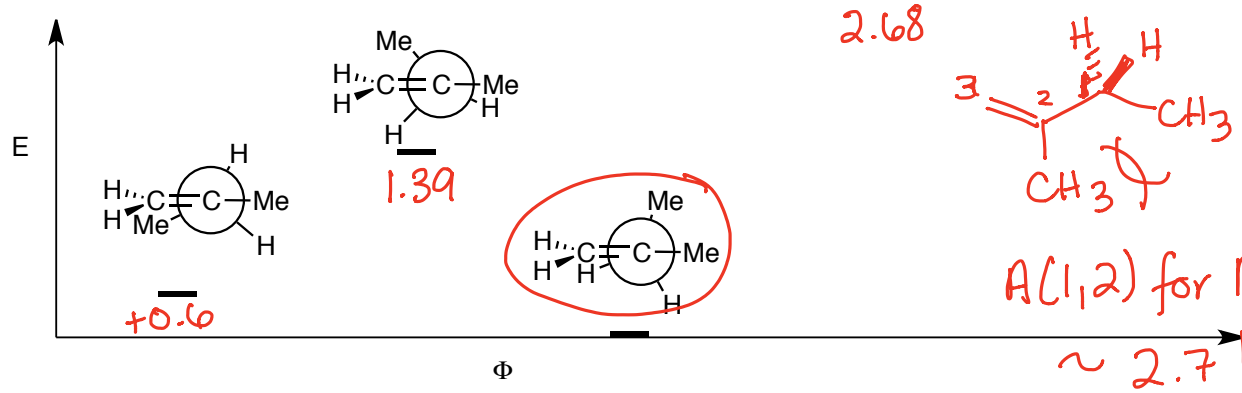


2-Methyl-1-Butene

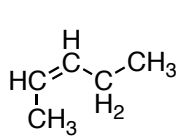


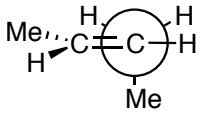


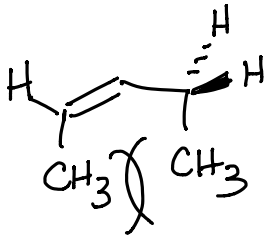




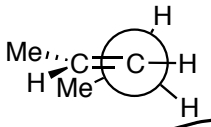
(*Z*)-2-pentene



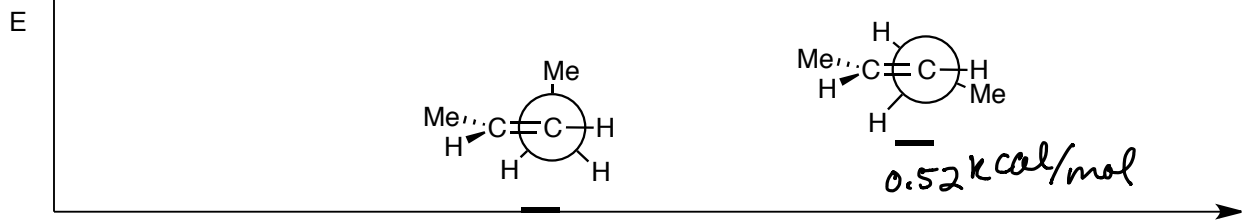




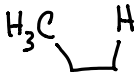
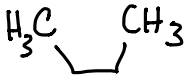
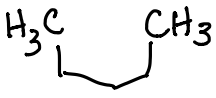
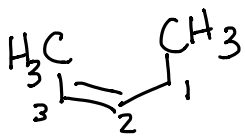
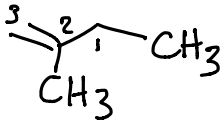
A (1,3) strain



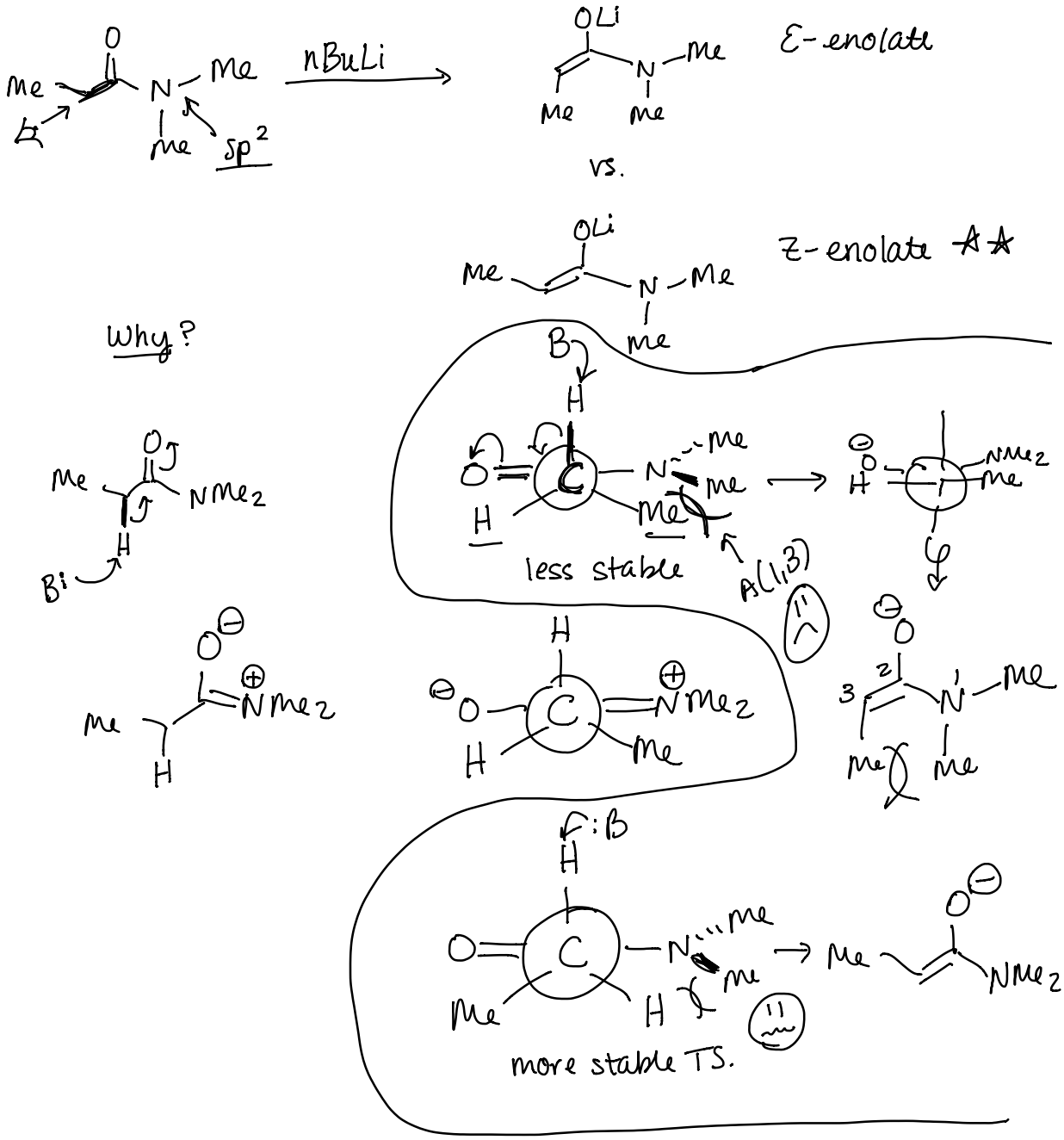
+3.88 kcal/mol



0.52 kcal/mol

Interaction	Energy (kcal/mol)	
	+1.0	
	1.4	
	3.1	
	3.7	syn-pentane or 1,3-diaxial if (acyclic) 6-membered ring
	0.88	gauche-butane or gauche-methyls
	4	A(1,3)
	2.7	A(1,2)

Amides always give (Z)-enolates.



Conformational Analysis of Cyclic Systems:

3 Types of Strain:

1) Prelog: van der Waals interactions
   STERIC

★ 2) Baeyer: bond angle distortion away from ideal.

3) Pitzer: torsional strain about a sigma bond

▷ Ideal: 109.5° 

Not possible in most rings.

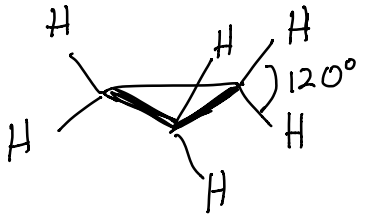
Table 2.15 in A&D
Table 2.3 in C&SA.

Take-home points: 1) 6-membered ring has least strain energy.

2) Cyclopropane: 27.5 kcal/mol.
   Cyclobutane: 26.3 kcal/mol.

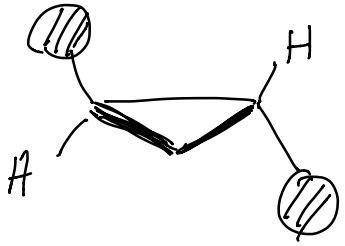
3) Medium-sized rings (n = 7–11)
   ↳ increase in strain but not angle strain.
      ↳ Transannular strain

Cyclopropane △



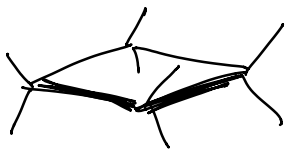
- planar
- substituents eclipsed

Disubstituted: trans is better.



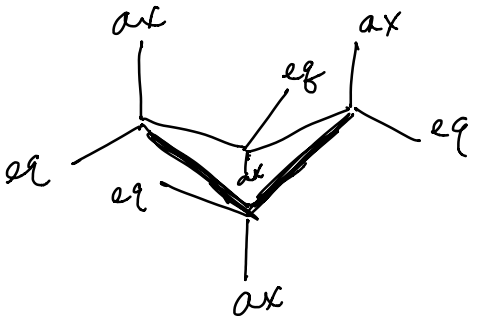
Cyclobutane

Planar? NO



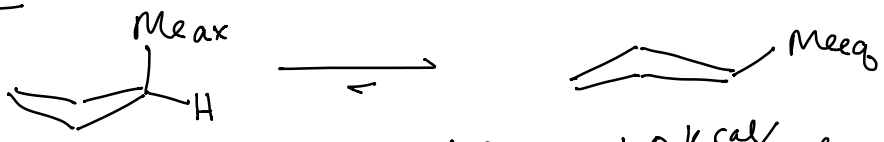
Lots of eclipsing bonds
↳ torsional strain

Pucker



Barrier to inversion: 1.45 kcal/mol
↳ flips easily @ rt

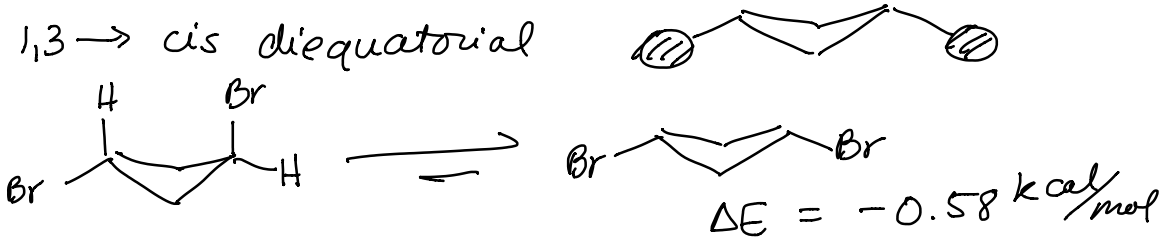
1 substituent



$\Delta G = -1.0$ kcal/mol

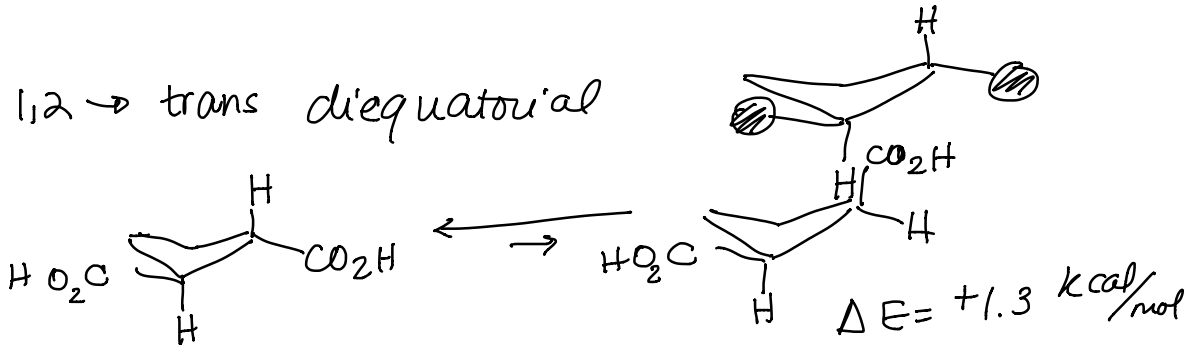
2 substituents

1,3 → cis diequatorial



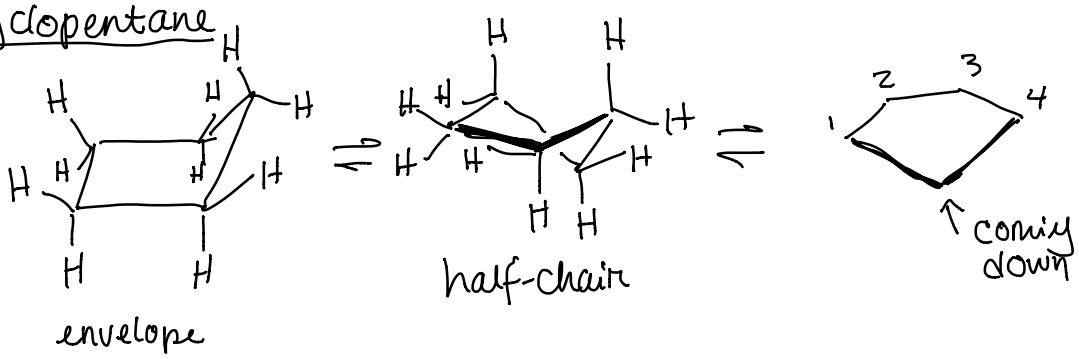
$\Delta E = -0.58$ kcal/mol

1,2 → trans diequatorial



$\Delta E = +1.3$ kcal/mol

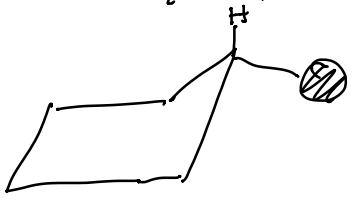
Cyclopentane



envelope ⇌ half-chair

↑ favored by 0.5 kcal/mol

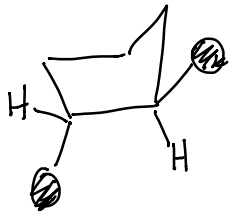
1 substituent:



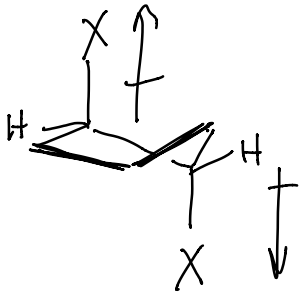
← eq. on envelope flap.

2 substituents:

1,2: Prefer trans

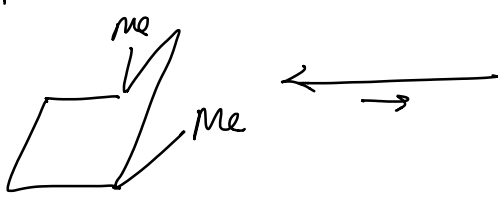


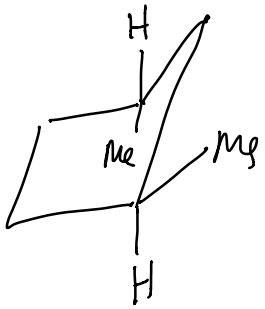
Steric/torsional reasons (alkyl)



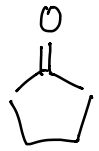
dipole reasons (polar groups)

1,3- prefers cis





$\Delta E = +0.5$ kcal/mol



prefers planar position in half chair
(also ⟨=CH2)

Their rationale: Oxygen adds to avoid steric hindrance w/ NH_2 & CO_2Me.

Are they right?