Lecture 9: Conformational Analysis of Rings

Announcements:

- *Midterm 1* is on Thurs, Sept 28!
  - Everything through conformational analysis of acyclic systems may be included (not today's lecture).
  - Exams from previous years are at the bottom of the course website.

- Problem Set 3 was graded for completion (not correctness). Please check your answers against the answer key posted on the course website.

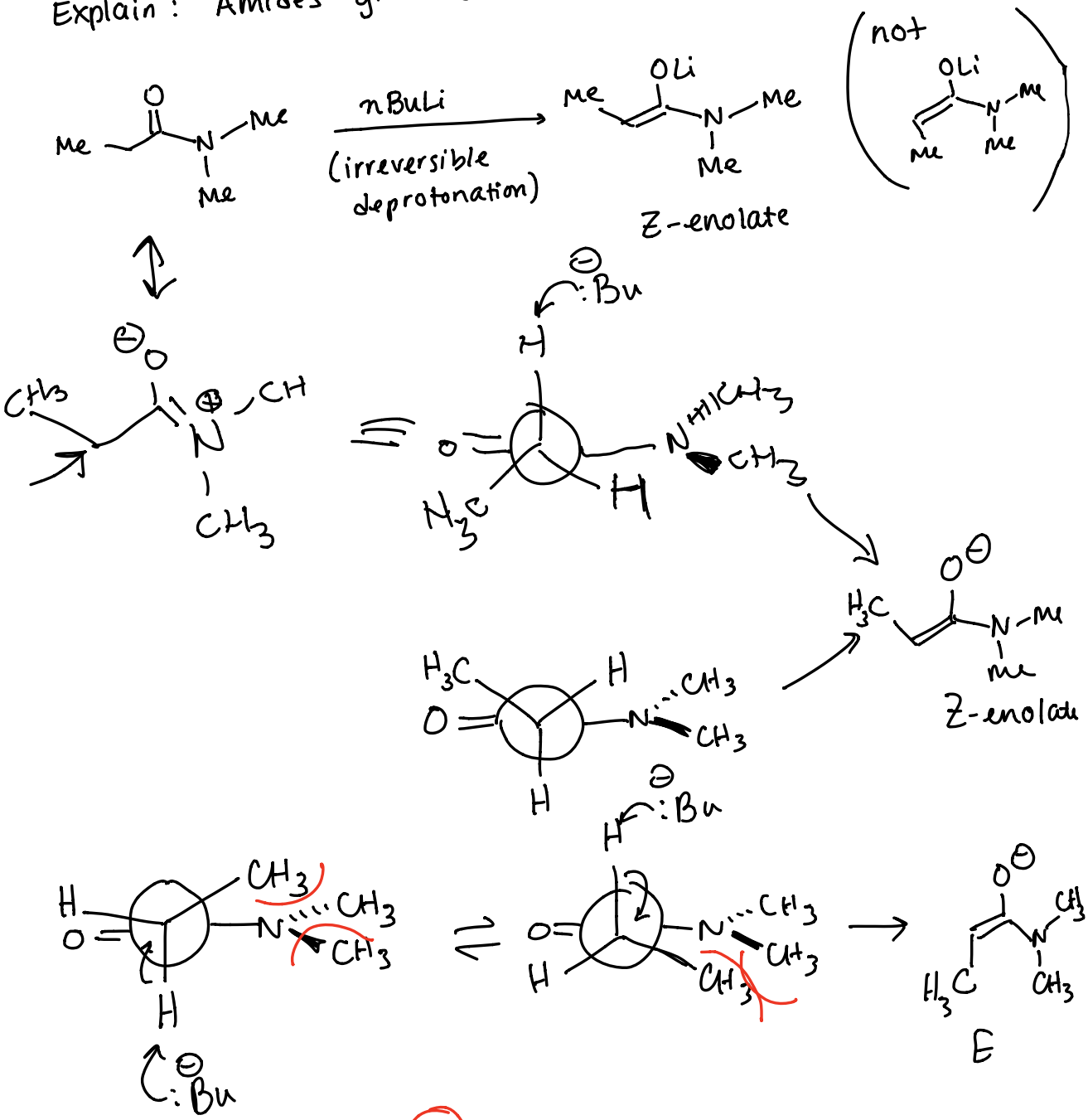
- Office Hour: Wed, 9:30-10:30am, 219 BRL. (Not 2:30-3:30). This week only.

Today:

- Amide question from last lecture
- Conformational analysis of rings
  - Types of strain
  - Ring strain vs. ring size
  - Conformations of rings

Practice Problem

Explain: Amides give (Z)-enolates.

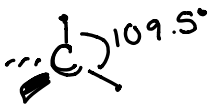


Conformational Analysis of Cyclic Systems

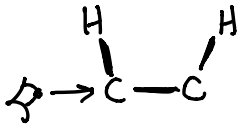
3 Types of Strain:

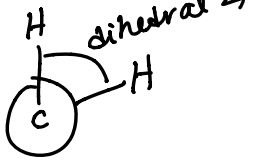
1) Prelog: van der Waals interactions ⇒ STERIC

*2) Baeyer: bond angle distortion away from ideal

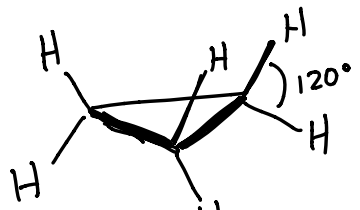
Ideal:  109.5° Not possible in most rings

3) Pitzer: torsional strain about a σ-bond



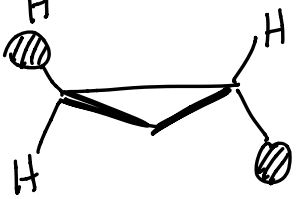


Cyclopropane △



- C's = planar
- substituents eclipsed

Disubstituted



trans is better.

Table 2.15
Strain Energies and Group Increment Correction Factors for Cycloalkanes, $(CH_2)_n$ (in kcal/mol)

n	Strain energy	Group increment	n	Strain energy
3	27.5	27.6	10	12.4
4	26.3	26.2	11	11.3
5	6.2	6.3	12	4.1
6	0.1	0	13	5.2
7	6.2	6.4	14	1.9
8	9.7	9.9	15	1.9
9	12.6	12.8	16	2.0

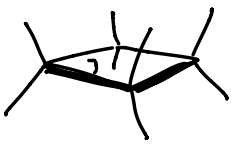
- most strain
- Least strain energy

From Anslyn & Dougherty.

Medium (7-11) → increase in strain, but not angle strain.
"transannular strain"

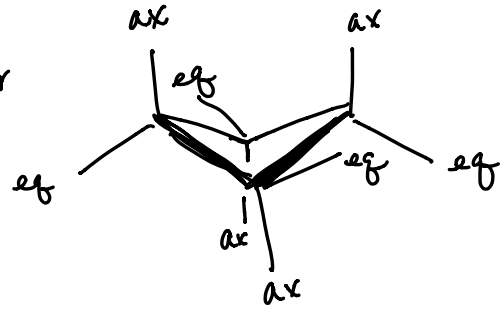
Cyclobutane

Planar?



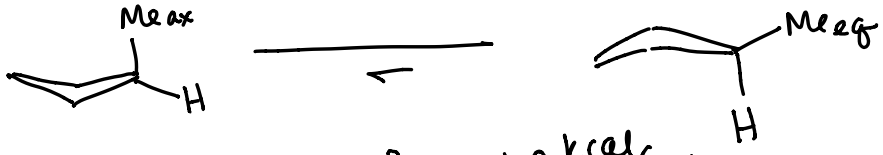
Lots of eclipsing bonds
↓
torsional strain

Pucker



Barrier to inversion
1.45 kcal/mol
↓
flips easily @ rt

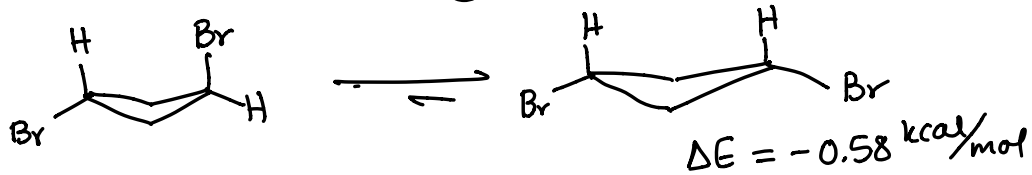
1-substituent:



$\Delta G^\circ = -1.0$ kcal/mol

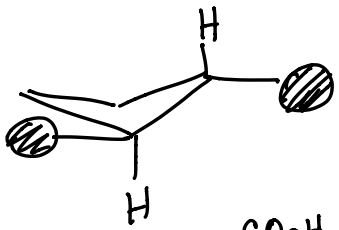
2 substituents

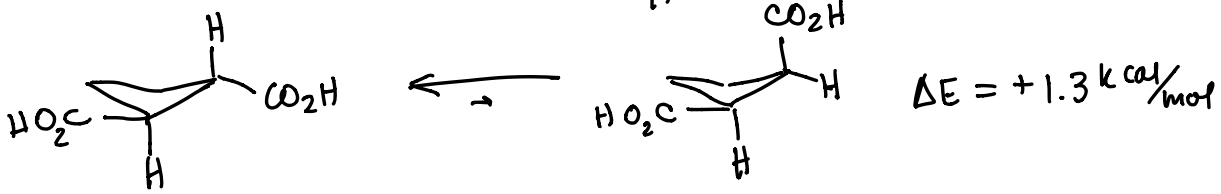
1,3 → cis diequatorial



$\Delta E = -0.58$ kcal/mol

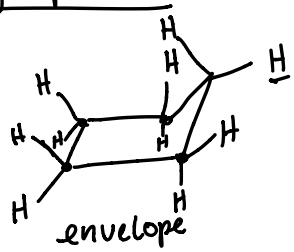
1,2 → trans diequatorial





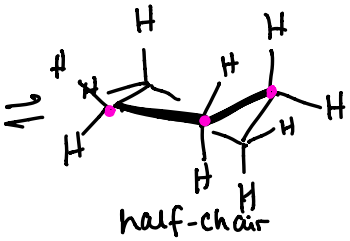
$\Delta E = +1.3$ kcal/mol

Cyclopentane



envelope

• = co-planar

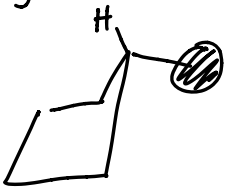


half-chair

• = co-planar

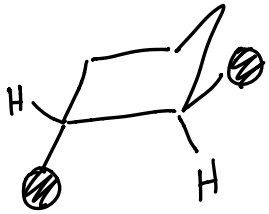
↑ favored by 0.5 kcal/mol

1 substituent :



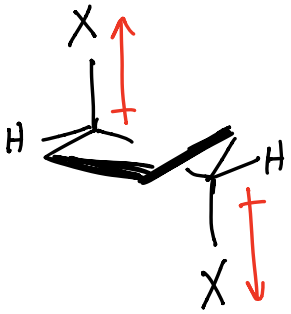
eq on envelope flap

2 substituents : 1,2 prefer trans



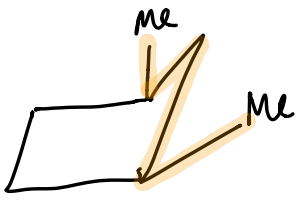
Steric/torsional reasons

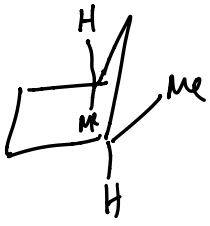
⊘ = alkyl



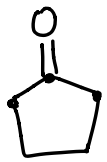
dipole reasons (polar groups)

1,3 - prefer cis



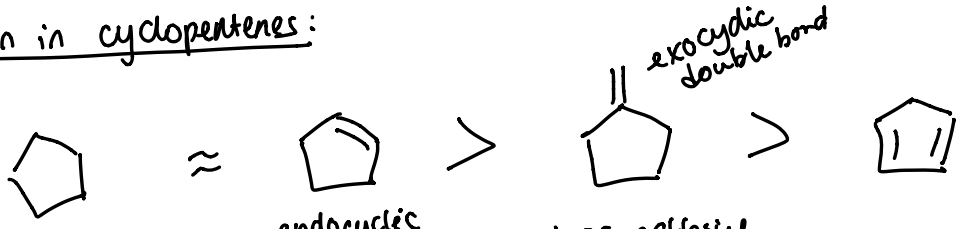


ΔE = +0.5 kcal/mol



sp^2 C prefers planar position of half chair

Strain in cyclopentenes:



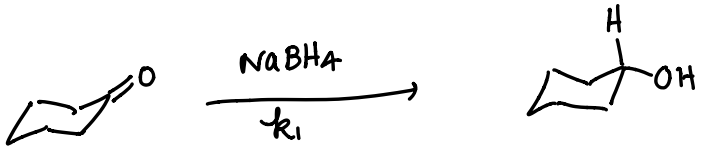
less eclipsing strain outweighs increase in angle strain.

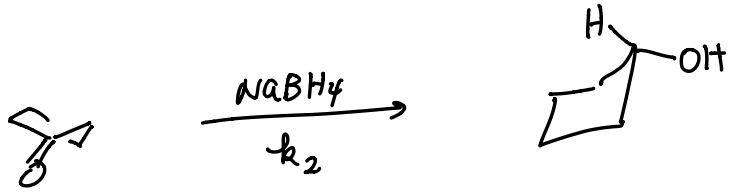
Cyclopentane derivatives → prefer sp^2 center in ring to minimize eclipsing interactions.

Rxns proceed to favor exo double bond.

In 6-membered rings: Rxns proceed to avoid exo double bond

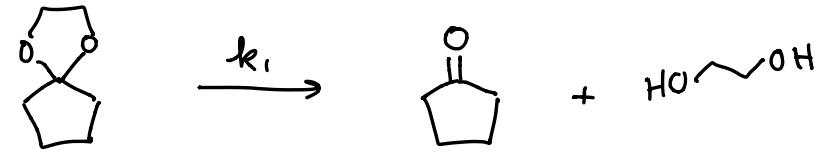
ex:

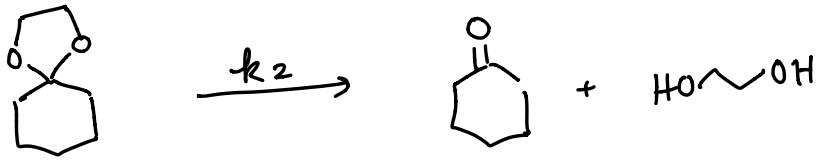




$\frac{k_1}{k_2} = 23$ Tetrahedron 1957, 221

ex:





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

Bull Soc Chim Fr 1976, 1935