Lecture 12: Conformational Effects (the end) & Kinetics (the beginning)

Announcements:

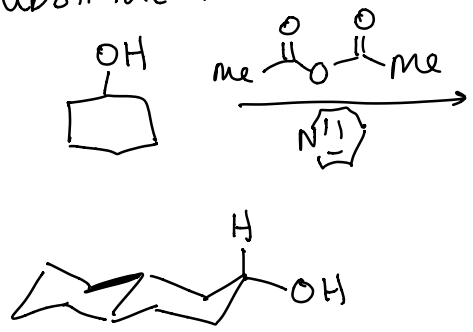
- Midterm 1 is not yet graded. Hopefully graded by Thursday.
- Problem Set 3 due Thurs, Oct 20. I will post it by this weekend.
- Seminar tomorrow: Dr. Martin Schnermann (National Cancer Institute)
  Wed, 4pm, 219 BRL
  "Remodeling the Cyanine Scaffold for New Applications in Drug Delivery and Imaging"

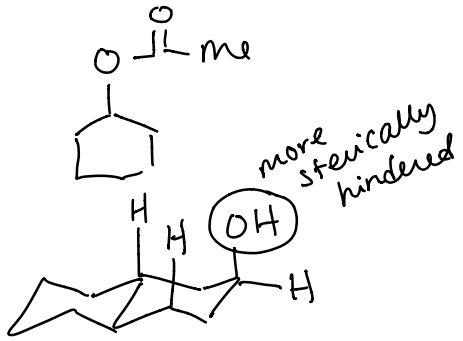
Today:

- Conformational Analysis to explain/predict reaction rates
- Thorpe-Ingold Effect
- Kinetics

Conformation Effects to explain rates.

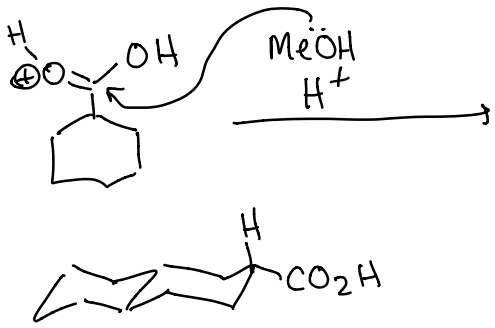
- Different reactivity for axial vs. equatorial substituents.

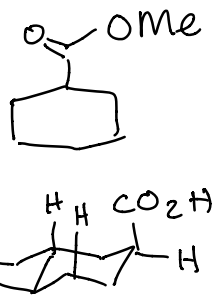




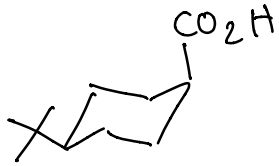
k_{rel} 1 0.13

In general, equatorial substituents react more quickly b/c less hindered.



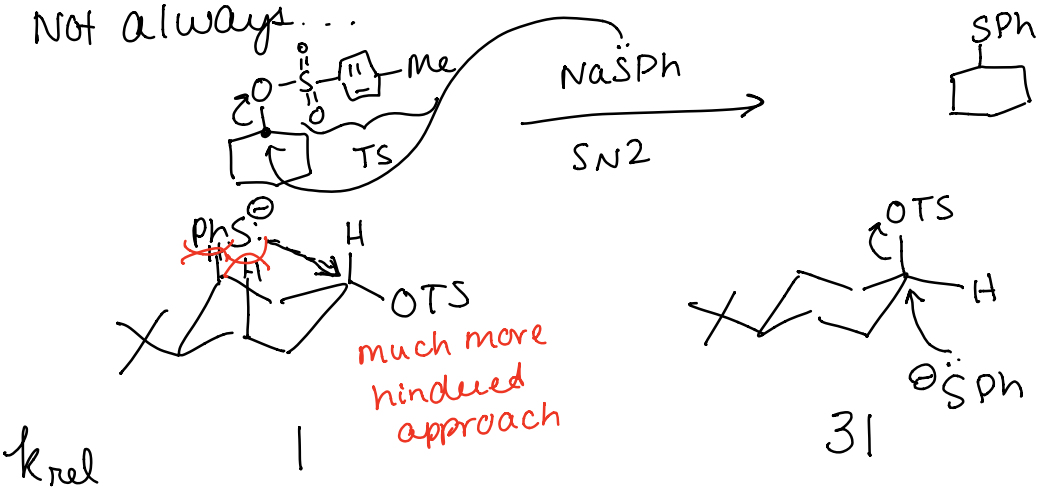


k_{rel} 1 0.04



k_{rel} 1 0.05

Not always...



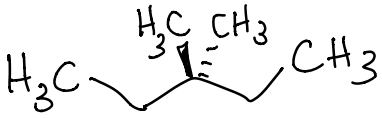
k_{rel} 1 31

Thorpe-Ingold Effect (Gem-dimethyl effect)

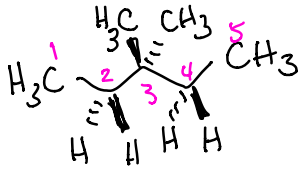
A & D, p. 496-497

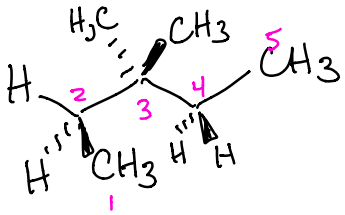
Geminal substitution accelerates cyclization reactions.

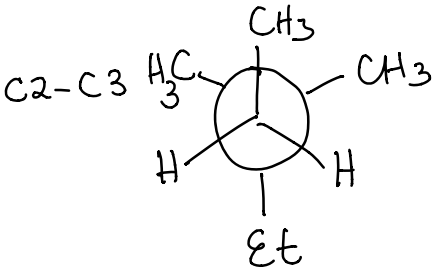
Consider : 



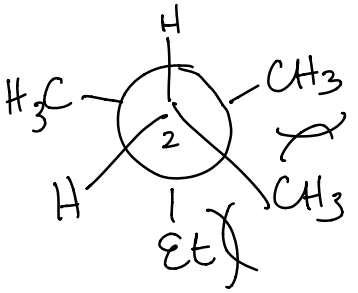
Possible Conformations:



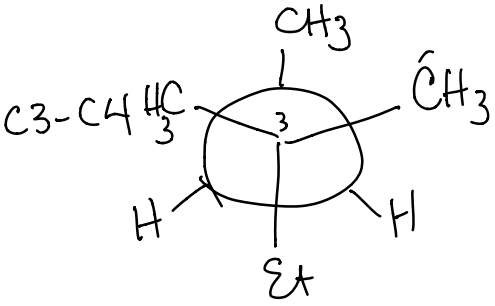




2GB's



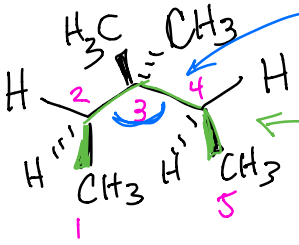
2GB's



2GB's

2GB's

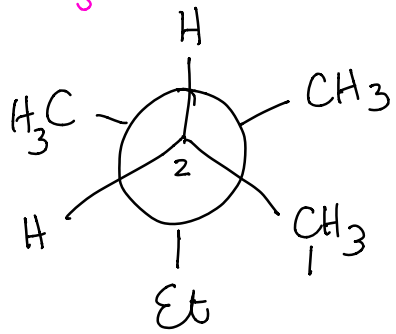
same as previous



slight angle compression.

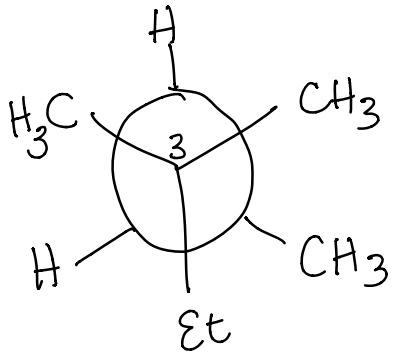
syn-pentane, too

C2-C3:



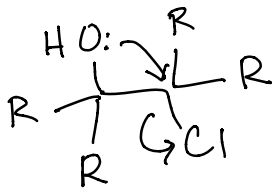
2 GB's

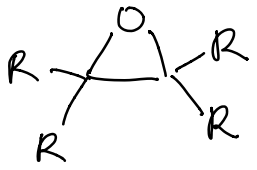
C3-C4:

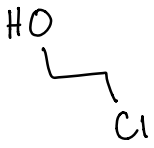
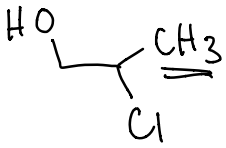
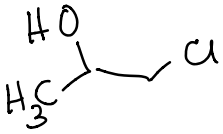
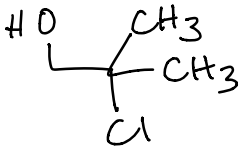
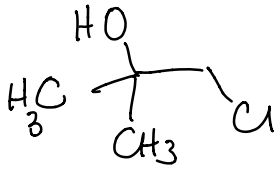
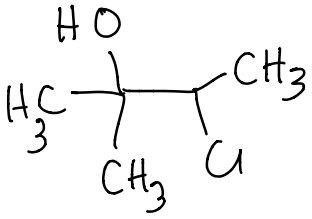


2 GB's

ex:





	krel
	1
	5.5
	21
	248
	252
	1360