① **Lecture 9: More Conformational Analysis**

Midterm Thursday: 3:30–6pm

You may use plastic models during the midterm.

Calculators will not be necessary.

②

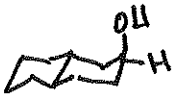
Conformational Effects to predict/explain rxn rates...

Different reactivity for axial vs. equatorial substituents.

Axial = more hindered, so often react more slowly...

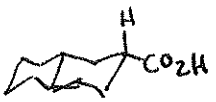
③

ex: Acetylation w/ Ac_2O/pyridine:

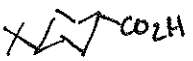


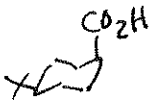
k_{rel} 1 0.13

④ ex: Acid-catalyzed Esterification



k_{rel} 1 0.04

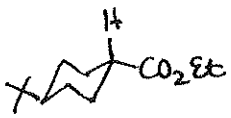


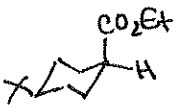


1 0.05

k_{rel}

⑤ ex: Ester saponification

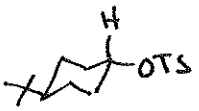


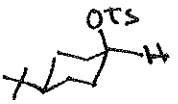


k_{rel} 20 1

⑥ But... Axial does not always react more slowly...

ex: S_N2 w/ $PhS^{\ominus}$





k_{rel} 1 31

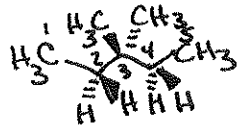
Consider angle of approach of nucleophile.

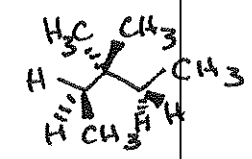
⑦ Thorpe-Ingold Effect / Gem-Dimethyl Effect

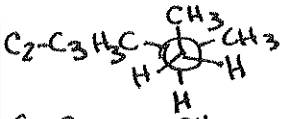
(A&D, p. 496-497.)

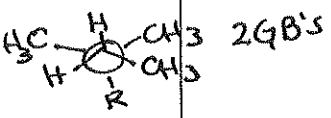
Consider 

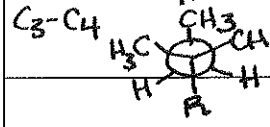
Possible Conformations:

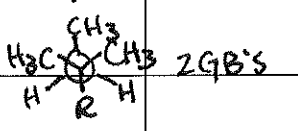




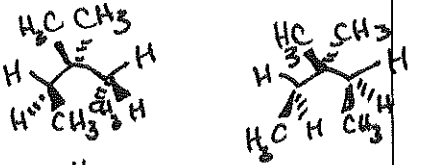


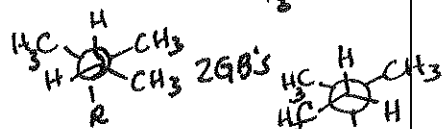


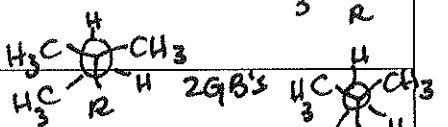




⑧



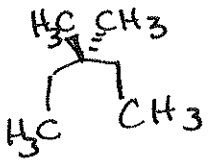




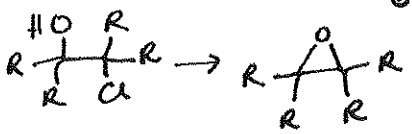
⑨ All ground state conformations are destabilized.

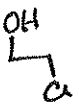
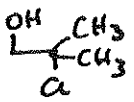
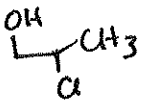
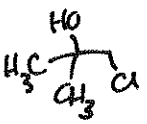
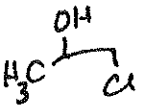
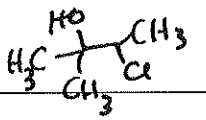
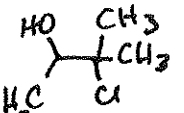
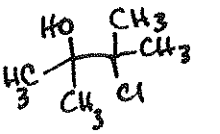
(Contrast w/  .)

Easier to get to



(also, slight angle compression)

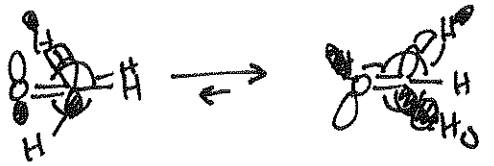
⑩ ex: 

	k_{rel}		k_{rel}
	1		248
	5.5		252
	21		1360
			2040
			11,600

Nilsson & Smith. Phys. Chem. 1933, 166A, 136.

⑪ PRACTICE PROBLEMS:

① Predict the most stable conformation of acetaldehyde. Use FMO analysis to support your prediction.



Destabilized by $\sigma_{CH} \leftrightarrow \pi_{CO}$

Stabilized by $\sigma_{CH} \leftrightarrow \pi^*_{CO}$

↑ also present in propene.

⑫