

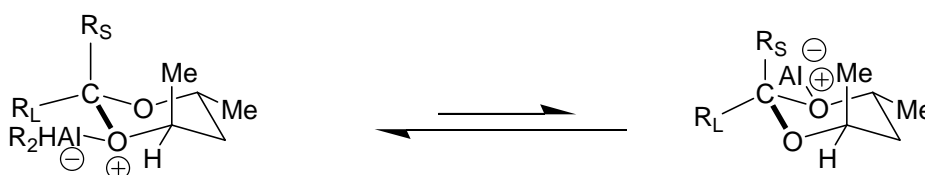
Lecture “Modern Synthetic Methods”

Take-home messages from Week 2

2.1.2. Conformational analysis of saturated heterocycles

- Acetals:**
- Cyclic acetals show higher A-values due to shorter bond length
 - Formation of oxonium species by Lewis acids (e.g. Prins cyclization)

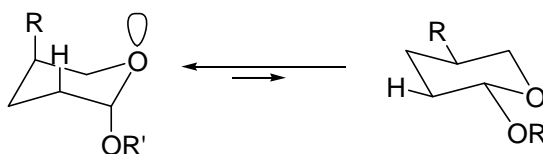
- Chiral acetals:**
- Opening to the oxonium species occurs in way which removes the greatest amount of unfavourable steric repulsion



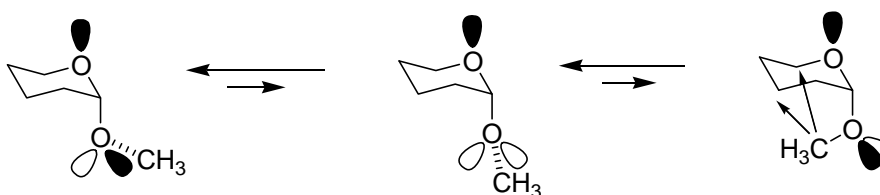
2.1.3. Stereoelectronic effects

Effects upon structure/reactivity by orbital interaction between σ/σ^* -orbitals and unfilled/filled orbitals on neighbouring centers.

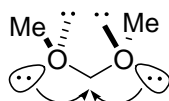
Endo anomeric effect: Electronegative substituents adjacent to oxygen prefer axial position



Exo anomeric effect: Rotation of OR group in anomeric position is “locked”



- Gauche effect:**
- Acyclic acetals prefer gauche conformation over linear conformation
 - Rotational barrier in esters and amides, higher reactivity of lactones compared to esters



- β -Silyl effect:**
- Silicon atoms stabilize carbocations at β -position

