

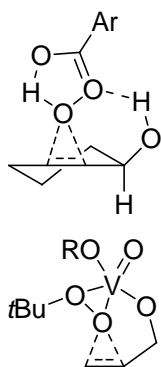
Lecture “Modern Synthetic Methods”

Take-home messages from Week 9

2.5. Diastereoselective Olefin Transformations

- General aspects:**
- Electrophilic reactions, higher substituted olefins react faster
 - Attack occurs perpendicular to C=C bond, **NOT** along Bürgi-Dunitz trajectory
 - Epoxidations, dihydroxylations and hydroborations are typically stereospecific *syn*-additions

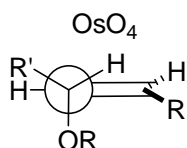
2.5.1. Epoxidations



- Most common reagents (i.e. mCPBA, VO(acac)₂/tBuO₂H) respond nicely to directing effects
- Directing groups include e.g. unprotected alcohols or amides
- Directing groups are essential for epoxidations using VO(acac)₂/tBuO₂H

2.5.2. Dihydroxylations

- OsO₄ is often used in catalytic amounts and Os(VI) reoxidized using NMO etc.
- Dihydroxylations of allylic alcohols (protected or unprotected) are often stereoselective, protecting groups have little influence **EXCEPT** acyl derivatives
- Three models: Vedejs, Houk/Stork, Kishi



- Kishi Model:** - Find most stable conformer minimizing A^{1,2}- or A^{1,3}-interactions
- OsO₄ attacks opposite OR group

2.5.3. Hydroborations

- Analysis more difficult, in addition to stereochemistry also regiochemical aspects
- Use of bulkier boranes can override A^{1,2}-repulsion

