SELECTIVITY

Science **1983**, *219*, 245

Chemoselectivity

preferential reactivity of one functional group (FG) over another

- Chemoselective reduction of C=C over C=O: H₂, Pd/C - Chemoselective reduction of C=O over C=C: OH NaBH₄ +NaBH₄, CeCl₃ only - Epoxidation: MCPBA OH ЮH ЮΗ (2:1)VO(acac)₂, tBuOOH exclusively ОН OH

Regioselectivity

- Hydration of C=C:



- Friedel-Crafts Reaction:



SELECTIVITY 2



Stereochemistry:

Relative stereochemistry: Stereochemical relationship between two or more stereogenic centers within a molecule

PhSH, (PhCO₂)₂

.SPh

R



syn: on the same side (cis) anti: on the opposite side (trans)

differences in relative stereochemistry lead to diastereomers.
Diastereomers= stereoisomers which are not mirror images; usually have different physical properties

Absolute Stereochemistry: Absolute stereochemical assignment of each stereocenter (R vs S) Cahn-Ingold-Prelog Convention (sequence rules)

- differences in absolute stereochemistry (of all stereocenters within the molecule) leads to enantiomers.

- Reactions can "create" stereocenters



Diastereomeric transition states- not necessarily equal in energy







Diastereoselectivity



Cram Model (Cram's Rule): empirical





SELECTIVITY 4

Felkin-Ahn Model



favored

disfavored

Chelation Control Mode



Stereospecific

Stereochemictry of the product is related to the reactant in a mechanistically defined manner; no other stereochemical outcome is mechanistically possible. i.e.; SN2 reaction- inversion of configuration is required



Stereoselective

When more than one stereochemical outcome is possible, but one is formed in excess (even if that excess is 100:0).



Diasteromers