

Review II, 2005: Chapters 20, 21, 22, 23

Mechanism:

NBS reaction: allylic bromination

acid catalyzed aldol

free radical substitution at the benzylic position

reactions with Huckel and Mobius transition states:

Diels Alder, Electrocyclic reactions, Sigmatropic

Shifts: Cope Rearrangement, Claisen Rearrangement,
hydride shifts

Electrophilic aromatic substitution

Nomenclature of bicyclic and
aromatic compounds

Spectroscopy of aromatic
compounds

Acidity and basicity

Structure of allylic cations, resonance hybrid

Kinetic versus Thermodynamic Control: reaction co-ordinate diagram

Structure and stereochemistry of cummulative π -bonds: allenes

Structure of Benzene: equal bond lengths, resonance hybrid

Aromaticity: $4n+2$ π electrons in a closed cycle of p-orbitals, other aromatic structures

Anti-aromaticity: $4n$ π -electrons in a closed cycle of p-orbitals

π -molecular orbitals for acyclic polyenes, allylic cations, anions and radicals

energy levels for π -molecular orbitals of aromatic and anti-aromatic structures

UV-Visible electronic absorption spectroscopy, Beer's Law

Reactions:

carbon-carbon bond forming reactions:

Wittig: allylic halide, PPh_3 , LiOEt , aldehyde

HCN to unsaturated ketone (catalyzed with AlEt_3)

Grignard with allylic halides

acid catalyzed aldol condensation

Grignard, RLi , LiCuR_2 , 1,2 versus 1,4 addition (nucleophilic addition)

Diels-Alder

Cope rearrangement/ Claisen rearrangement (6-electron Huckel transition state)

Electrocyclic ring closing (and opening) reactions: Huckel and Mobius transition states

Friedel Crafts alkylation (rearrangements and multiple substitutions can occur)

Friedel Crafts acylation (with Wolff Kishner yields alkyl substitution)

substitution reactions:

free radical bromination at the benzylic position

free radical bromination at the allylic position with NBS

electrophilic substitution of a proton on an aromatic compound for Cl, Br, NO₂, alkyl, acyl

(remember o/p activating, o/p deactivating, and m deactivating groups; resonance structures of intermediates as models for transition states; free energy diagrams; meta director blocks the Friedel Crafts reactions)

redox reactions:

1,2- versus 1,4-reduction of unsaturated ketones and aldehydes with NaBH₄ and LiAlH₄

catalytic hydrogenation, particularly hydrogenolysis at the benzylic position

Birch reduction (sodium in liquid ammonia) gives 1,4-dihydrobenzene

Oxidation of allylic and benzylic alcohols to aldehydes

Wolff-Kishner (hydrazine/KOH); Clemmensen (Zn/Hg/HCl); both, ketone or aldehyde to hydrocarbon