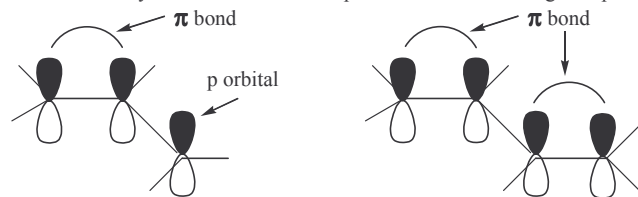


Summary of CH14 Delocalized π Systems

I. Definition

Delocalized π systems: extended overlap of three or more contiguous p orbitals



Allylic systems (C^+ , C^\bullet , C^-)

Conjugated dienes

II. Stability of delocalized π -systems

π -electron delocalization stabilizes the entire π -system

C^+ : substituted allylic $> 3^\circ > \text{allyl} > 2^\circ > 1^\circ$

C^\bullet : substituted allylic or allyl $> 3^\circ > 2^\circ > 1^\circ$

C^- : $\text{CH}_2=\text{CH}-\text{CH}_2^- > \text{CH}_3-\text{CH}_2-\text{CH}_2^-$

• Review resonance theory

-know how to draw resonance structures and determine their relative stabilities.

-explain the formal charge (C^+ , C^\bullet , C^-) distribution in a delocalized π -system

-know how resonance structures contribute to the stability of the actual molecule

• MO theory

-numbers of AOs is equal to numbers of MOs

-node and its relationship to stability of MO

-explain the formal charge (C^+ , C^\bullet , C^-) distribution according to individual MO

-Fill up the bonding MOs with π electrons lowers the energy of the π system (stabilization)

III. Kinetic vs. Thermodynamic control

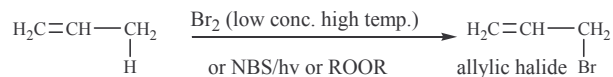
• Kinetic control: the ratio of products of a reaction is determined by the relative rate.

• Conditions favor kinetic control: short reaction time, lower reaction temp, irreversible reactions

• Thermodynamic control: the ratio of products of a reaction that reaches equilibrium is determined by the relative stabilities of the products

• Conditions favor thermodynamic control: longer reaction time, higher reaction temperature, reversible reactions

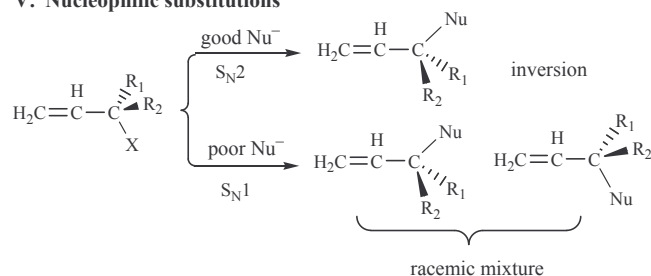
IV. Allylic halogenation



• Radical substitution (favored by the formation of an allylic radical) vs. ionic addition

• NBS in the presence of ROOR or hv (radical mechanism) gives exclusive allylic bromination

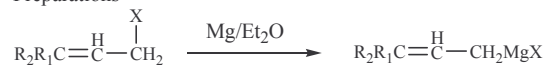
V. Nucleophilic substitutions



1° or 2° allylic halides undergo S_N1 reactions with poor nucleophiles and S_N2 reactions with good nucleophiles and 3° allylic halides always undergo S_N1 reactions.

VI. Allylic Grignard and allyllithium reagents

• Preparations



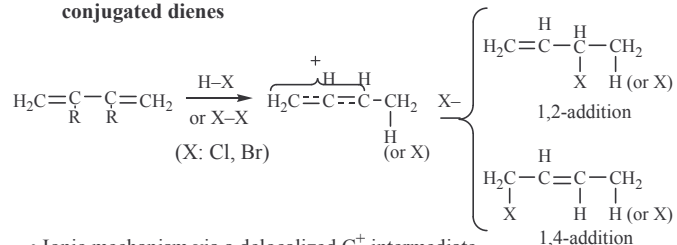
allylic halide allylic Grignard



allyllithium

• Allylic Grignard and allyllithium reagents react with electrophiles like other organometallic compounds.

VII. Electrophilic 1,2 vs 1,4-additions of H-X or X_2 to conjugated dienes

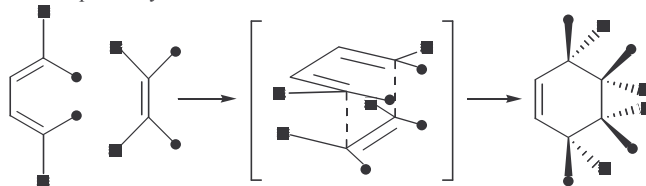


• Ionic mechanism via a delocalized C^+ intermediate

• 1,2-addition is the kinetic product while 1,4-addition is the thermodynamic product

VIII. Diels-Alder cycloadditions

• Diels-Alder reaction is a concerted reaction with a high stereospecificity



• Kinetically controlled addition favors endo products while thermodynamically controlled addition favors exo products.

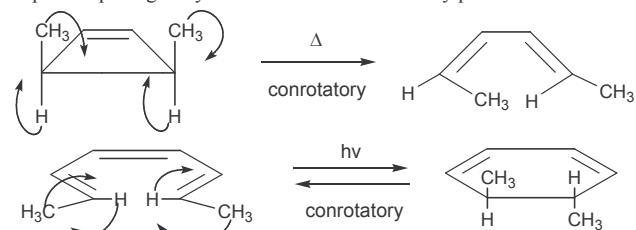
• Most Diels-Alder reactions are reversible.

IX. Electrocyclic reactions

• Electrocyclic reactions are concerted and the stereospecificities of these reactions are governed by the symmetry properties of the π MOs.

• Conrotatory: groups bonded to the termini of the final diene system rotate in the same direction.

• Thermo-opening of cyclobutene and photocyclization of hexatriene or photo-opening of cyclohexadiene are conrotatory processes.



• Disrotatory: groups bonded to the termini of the final diene system rotate in the opposite direction

• Photocyclization of butadiene or thermo-opening of cyclobutene and thermocyclization of hexatriene are disrotatory processes.

