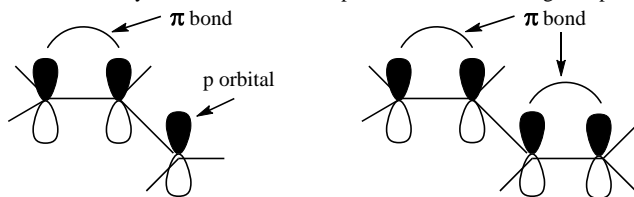


Summary of CH14 Delocalized π Systems

I. Definition

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



Allylic systems (C^+ , C^* , 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^* : 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^* , 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

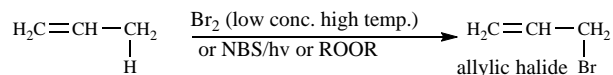
-explain the formal charge (C^+ , C^* , C^-) distribution according to individual MO

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

III. Kinetic vs. Thermodynamic control

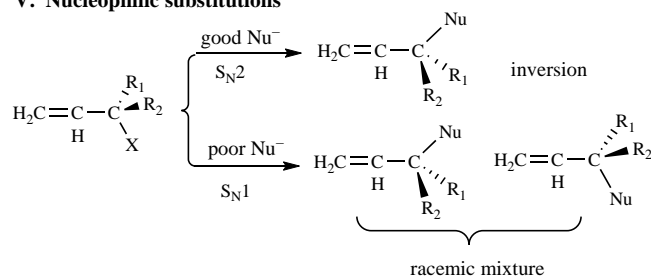
- Kinetic control: the ratio of products of a reaction is determined by the relative rate.
- Conditions favor kinetic control: short reaction time, lower reaction temp, irreversible reactions
- Thermodynamic control: the ratio of products of a reaction that reaches equilibrium is determined by the relative 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

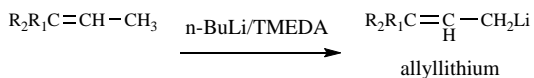
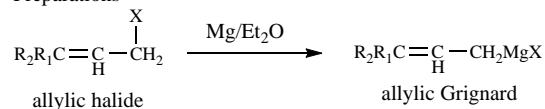
V. Nucleophilic substitutions



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

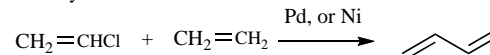
- Preparations



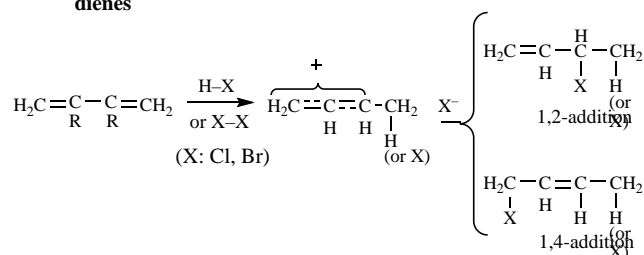
- Allylic Grignard and allyllithium reagents react with electrophiles like other organometallic compounds.

VII. Conjugated Dienes

Synthesis The Heck Reaction



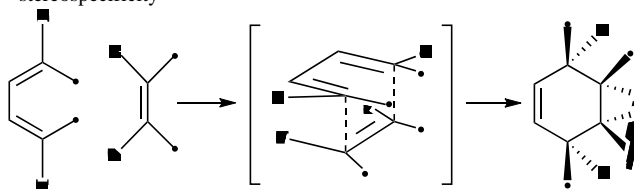
VIII. Electrophilic 1,2 vs 1,4-additions of H-X or X_2 to conjugated dienes



- Ionic mechanism via a delocalized C^+ intermediate
- 1,2-addition is the kinetic product while 1,4-addition is the thermodynamic product

IX. 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.

X. Intra molecular Electrocyclic reactions

