Conjugated Systems
Synthesis and Reactions

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Synthesis of Conjugated Systems

• Elimination reactions are used to make alkenes and can be extended to make conjugated compounds.

• Start from a dibromo compound and do two eliminations:

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Br Br
Br
Br
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\[ \text{tBuO}^+\text{K}^+ \xrightarrow{\Delta} \text{Br} \]

• Start from an alkene – add bromine in allylic position and then do elimination.

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\text{Br}
\text{Br}
\text{Br}
\text{Br}
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\[ \text{EtO}^-\text{Na}^+ \xrightarrow{\Delta} \text{Br} \]

\[ \text{NBS} \]

\[ \text{EtO}^-\text{Na}^+ \xrightarrow{\Delta} \]
Addition Reactions on Conjugated Dienes

- Electrophilic addition on the double bond.

- There must be some resonance going on in the intermediate, the allylic cation.

- Nucleophile adds to either carbon 2 or 4, both of which have the delocalized positive charge.

\[ \text{Conjugated System Synthesis and Reactions} \]
Addition of HBr: Kinetic Vs Thermodynamic

$$\text{H}_2\text{C} = \text{C} \quad \text{C} = \text{CH}_2 \quad + \quad \text{H}^+ \quad \rightarrow \quad \text{H}_3\text{C} \quad \text{C} \quad \text{C} = \text{CH}_2 \quad + \quad \text{Br}^-$$

*Kinetic product*  
1,2-addition product

$$\text{H}_3\text{C} \quad \text{C} \quad \text{C} = \text{CH}_2 \quad \text{Br}^-$$

1,4-addition product

*Thermodynamic product*

Major product at 40°C

Major product at -80°C

1,4-product (more stable)

(formed faster)
Kinetic and Thermodynamic Products..2

- Addition to a conjugated diene at or below room temperature normally leads to a mixture of products in which the 1,2 adduct (kinetic product) predominates over the 1,4 adduct (thermodynamic product).

- At higher temperature, the product ratio changes and the 1,4 adduct (thermodynamic) predominates.

1,3-Butadiene

1,2-Adduct

1,4-Adduct

At 0 °C: 71%
At 40 °C: 15%

29%
85%
Allylic Cations and Radicals

**Cation**
- Carbon adjacent to C=C is allylic.
- Allylic cation is stabilized by resonance.
- Stability of 1° allylic $\approx$ 2° carbocation.
- Stability of 2° allylic $\approx$ 3° carbocation.

**Radicals**
- Stabilized by resonance.
- Radical stabilities: 1° < 2° < 3° < 1° allylic.
- Substitution at the allylic position competes with addition to double bond.
- To encourage substitution, use a low concentration of reagent with light, heat, or peroxides to initiate free radical formation.
Allylic Bromination

- Bromination occurs at the allylic carbon.
- Mechanism is by free radical.

\[ \text{Br}_2 \xrightarrow{h\nu} 2 \text{Br}^- \]

\[ \text{H}_2\text{C} = \text{C}(\text{H}) = \text{C} = \text{C} = \text{CH}_2 \xrightarrow{\text{Br}^-} \]

- \textit{N-Bromosuccinimide} (NBS) provides a low, constant concentration of \text{Br}_2.
- NBS reacts with the HBr by-product to produce \text{Br}_2 and prevent HBr addition.

\[ \text{HBr} + \text{N-Br} \rightarrow \text{Br}_2 + \text{N-H} \]

N-bromosuccinimide (NBS)     succinimide
Key Concepts

• Kinetic and Thermodynamic additions
• Resonance
• NBS – allylic additon