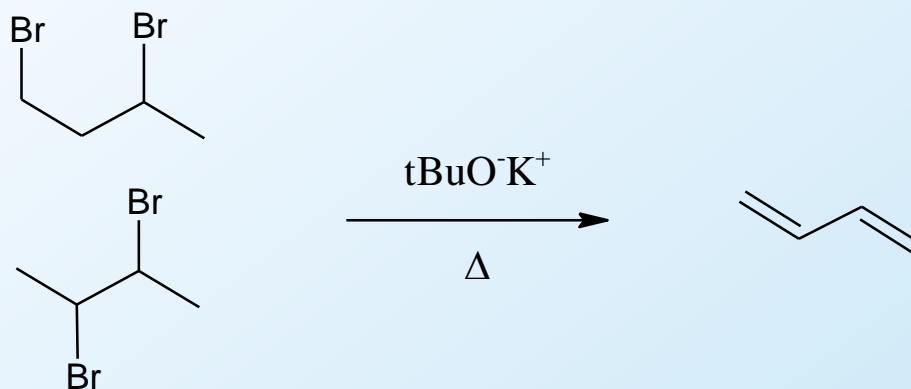


Conjugated Systems Synthesis and Reactions

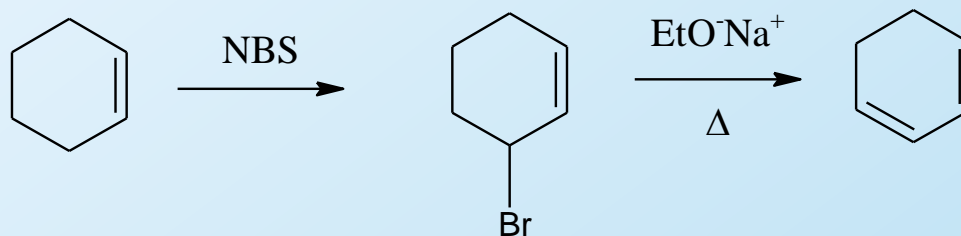
Dr. Sapna Gupta

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:

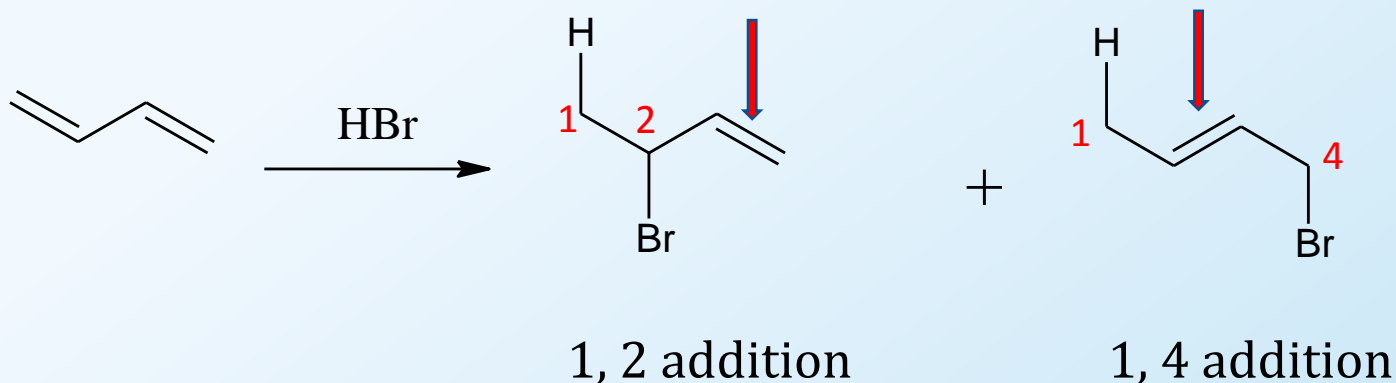


- Start from an alkene – add bromine in allylic position and then do elimination.



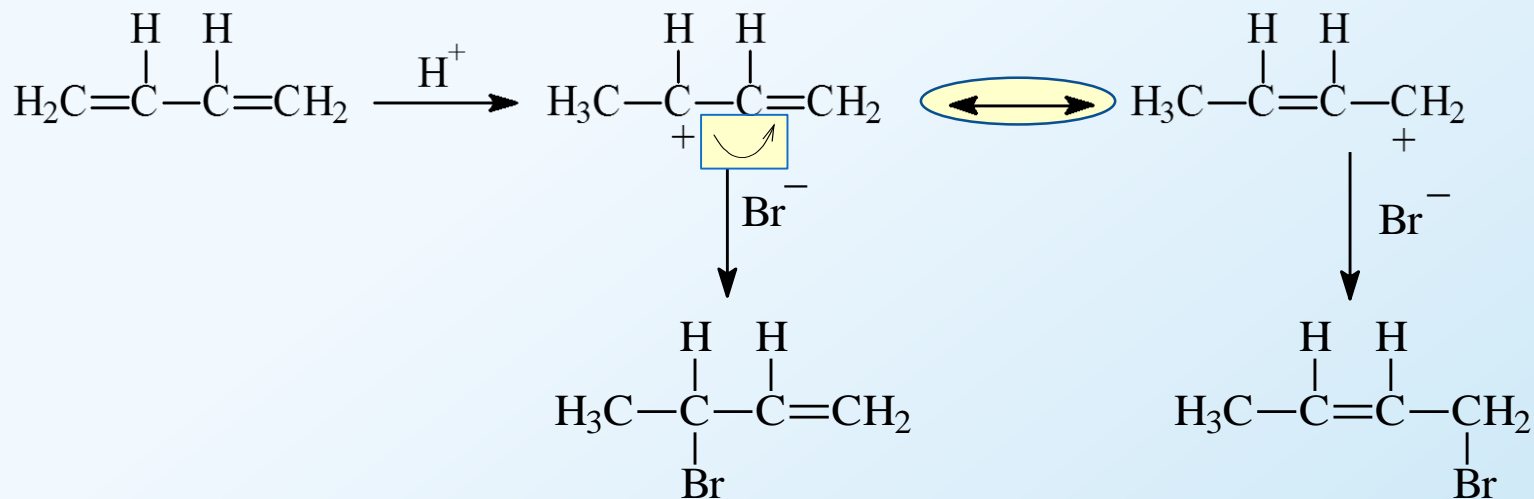
Addition Reactions on Conjugated Dienes

- 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.

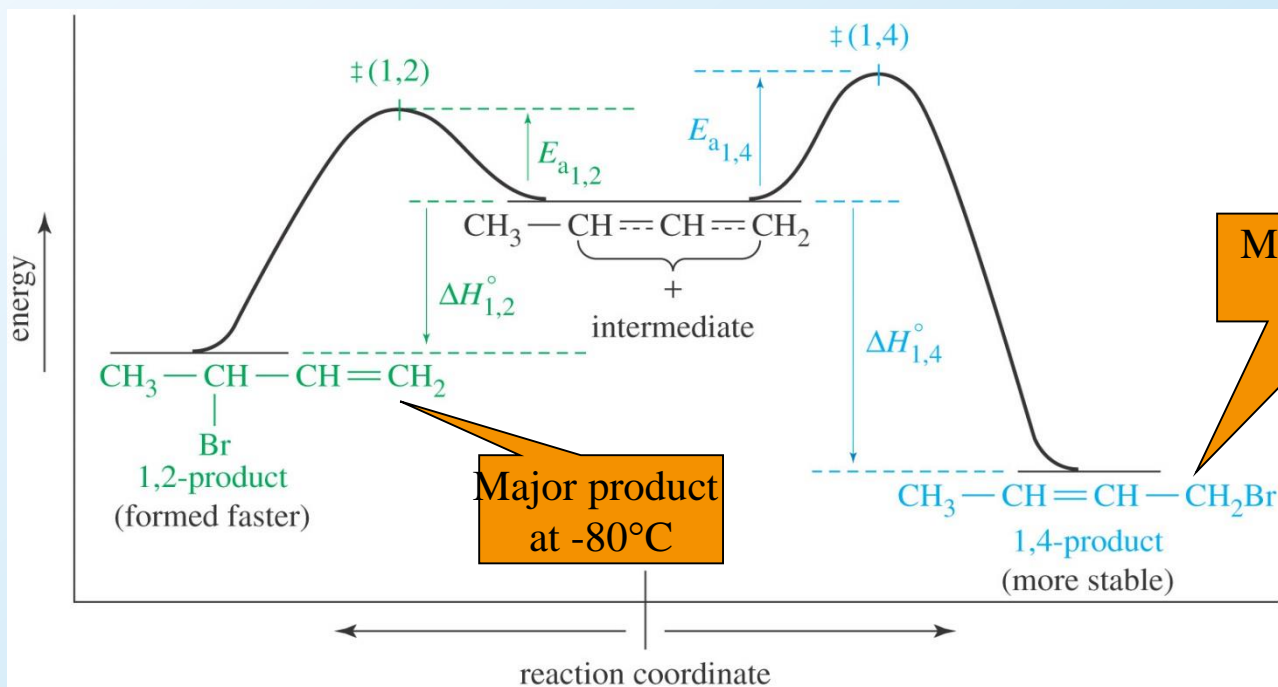
Addition of HBr: Kinetic Vs Thermodynamic



Kinetic product 1,2-addition product

1,4-addition product

Thermodynamic product

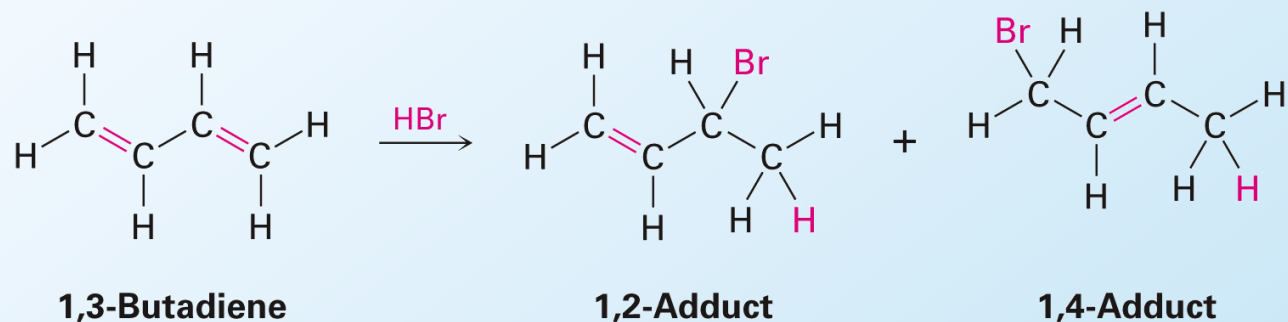


Major product
at 40°C

Major product
at -80°C

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

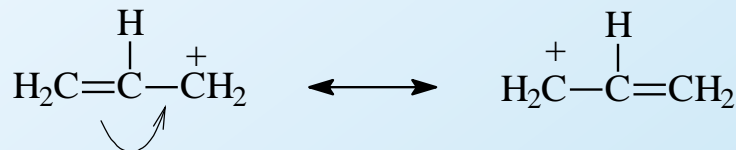


At 0 °C:	71%	29%
At 40 °C:	15%	85%

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.

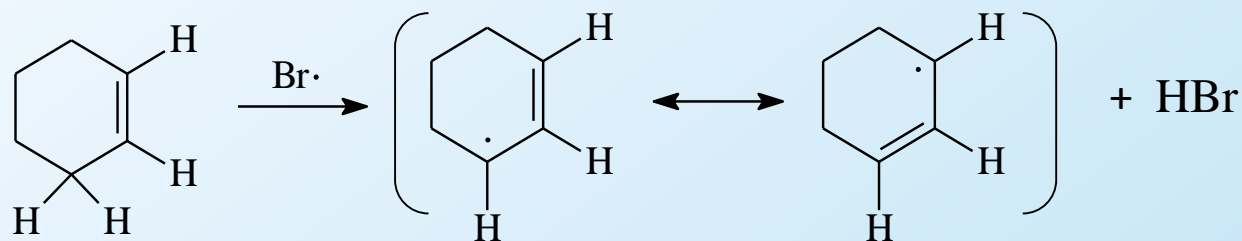
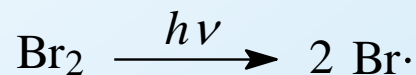


Radicals

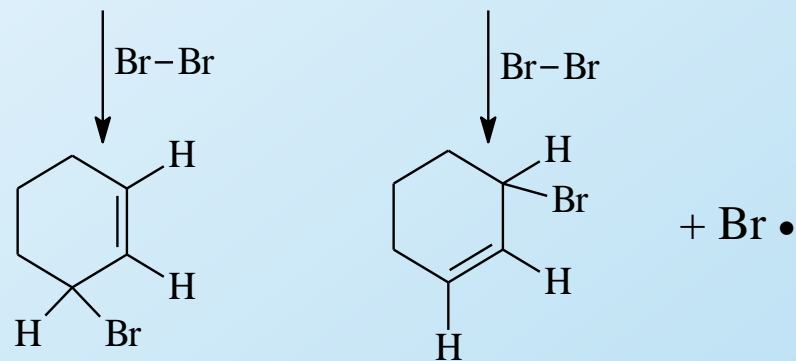
- Stabilized by resonance.
- Radical stabilities: 1° < 2° < 3° < 1° allylic.
- Substitution at the allylic position competes with addition to double bond.
- To encourage substitution, use a low concentration of reagent with light, heat, or peroxides to initiate free radical formation.

Allylic Bromination

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



- **N-Bromosuccinimide (NBS)** provides a low, constant concentration of Br_2 .
- NBS reacts with the HBr by-product to produce Br_2 and prevent HBr addition.



Key Concepts

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