Conjugated Systems
2 - Synthesis and Reactions

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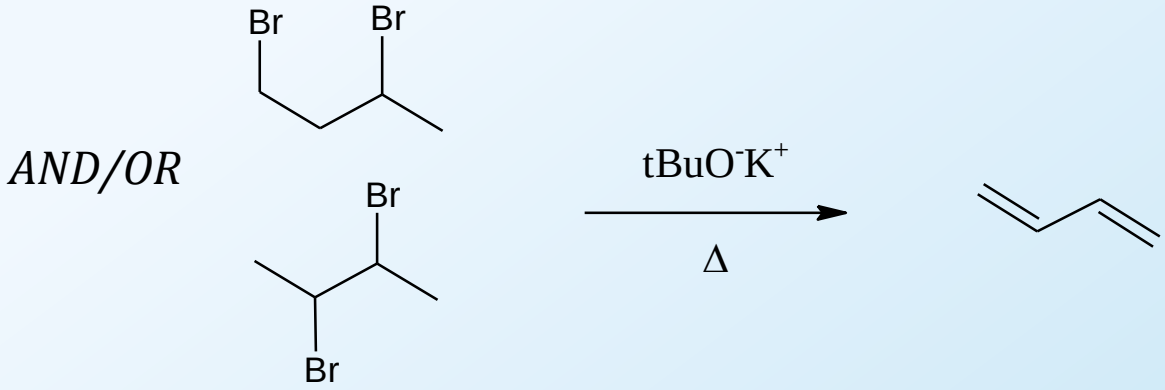
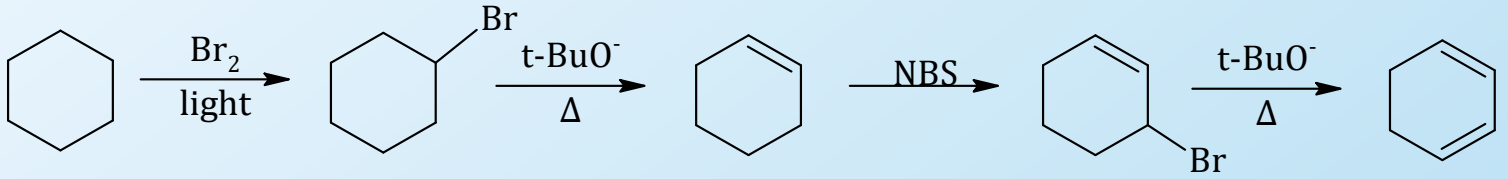
Synthesis of Conjugated Systems

Elimination reactions, usually E2, are used to make alkenes and can be extended to make conjugated compounds. We cannot use diols to carry out eliminations (E1).

- Start from a dibromo compound and do two eliminations:

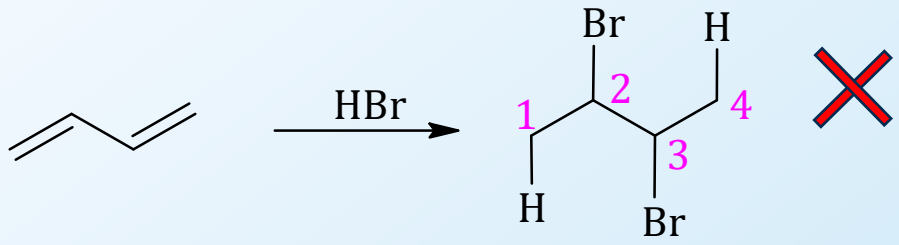


- Start from an alkane or alkene, add bromine in allylic position and then carry out elimination.

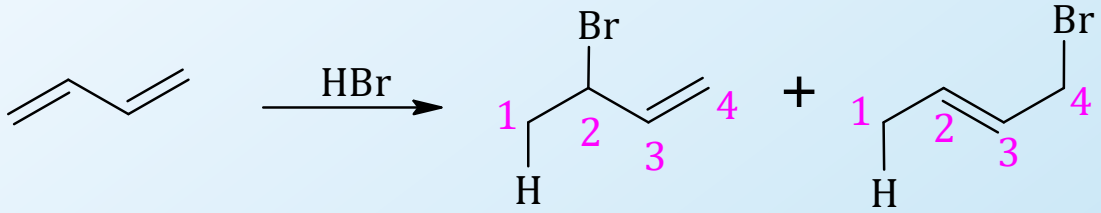


Reaction on Conjugated Dienes

All reactions on alkenes are addition and conjugated dienes are not different. Electrophilic addition on the double bond. When addition on an alkene is carried out, a 1,2- addition product is produced. When a diene is treated with HBr, the product shown below should be obtained.



However, in reality, the products below are obtained.

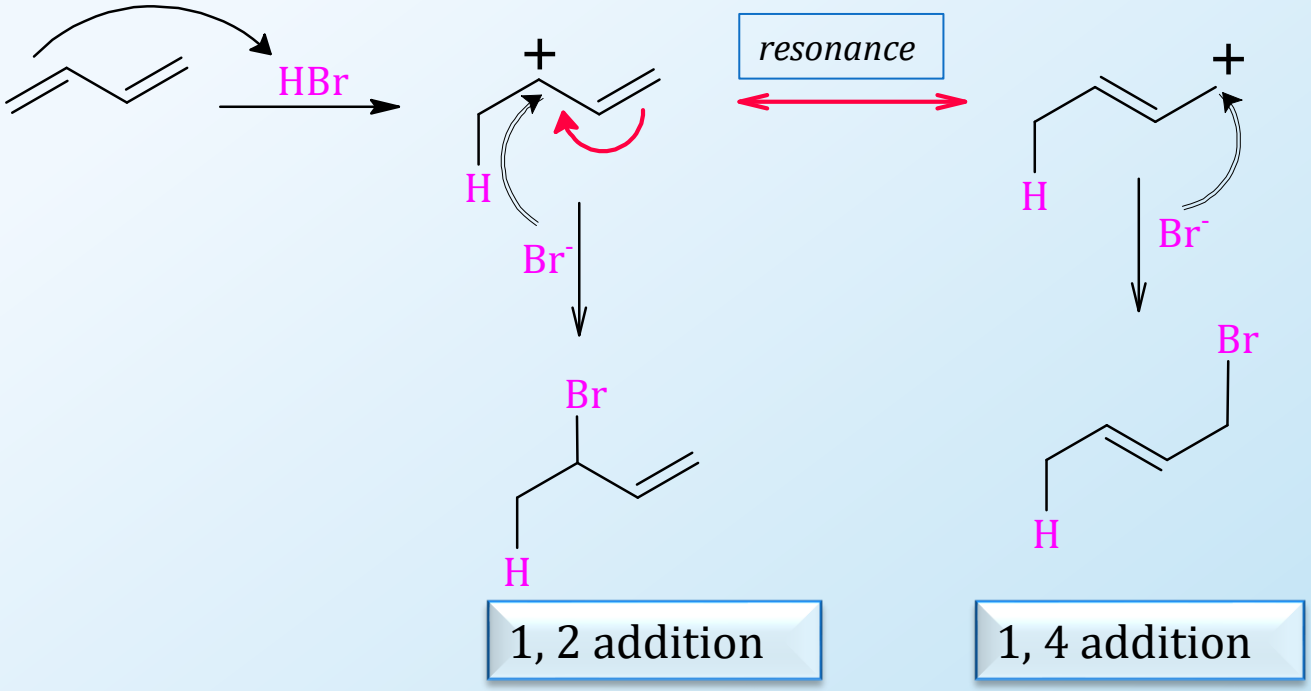


1, 2 addition 1, 4 addition

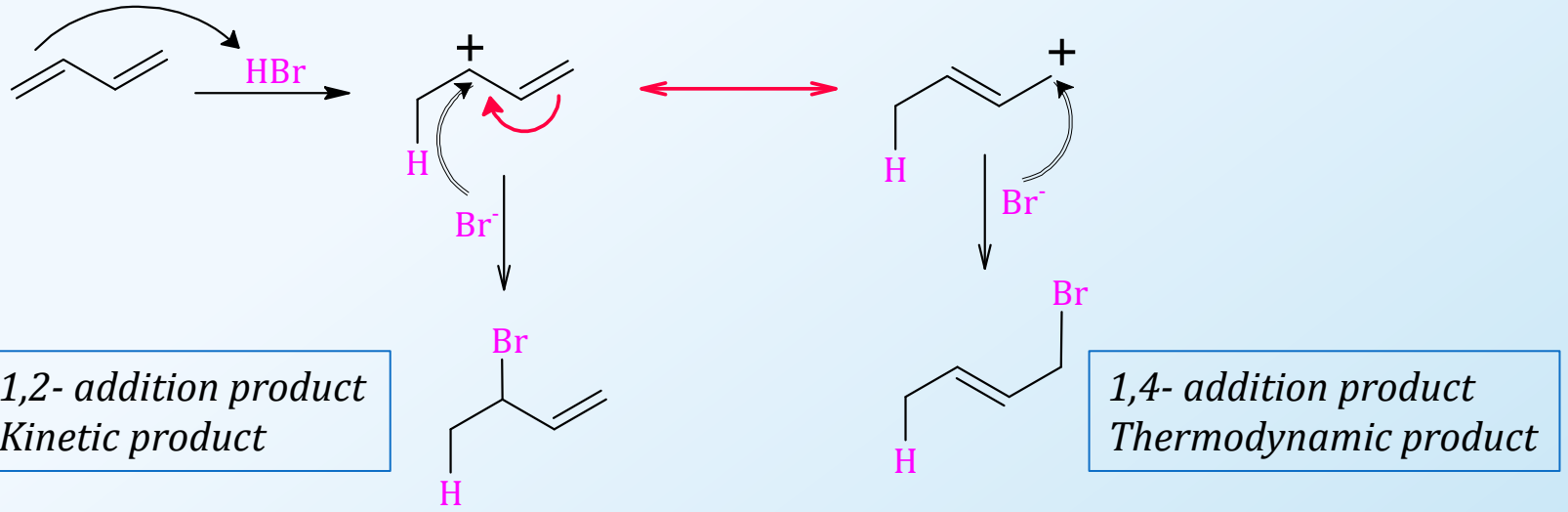
This indicates that there must be some other mechanism going on for us to get two products with a 1,2- and a 1,4-addition.

Mechanism and Explanation

The products can be explained by the mechanism below. It starts with the usual electrophilic attack on acidic proton by the double bond (Nu). Once the carbocation forms, the presence of the conjugated double bond causes resonance, forming two cations.



Addition of HBr: Kinetic Vs Thermodynamic



1,2- addition product
Kinetic product

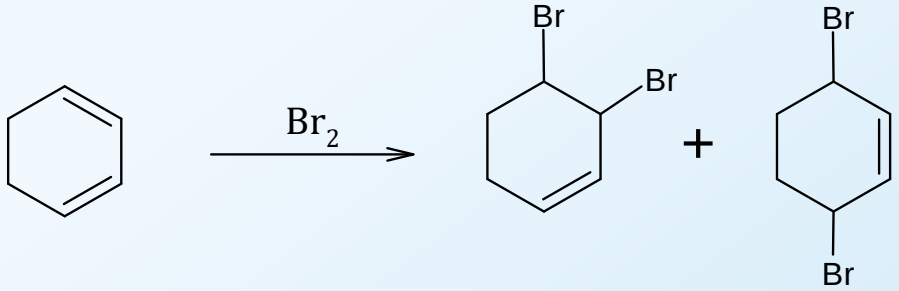
1,4- addition product
Thermodynamic product

	Major product at -80°C	Major product at 40°C
At 0°C	70%	30%
At 40°C	15%	85%

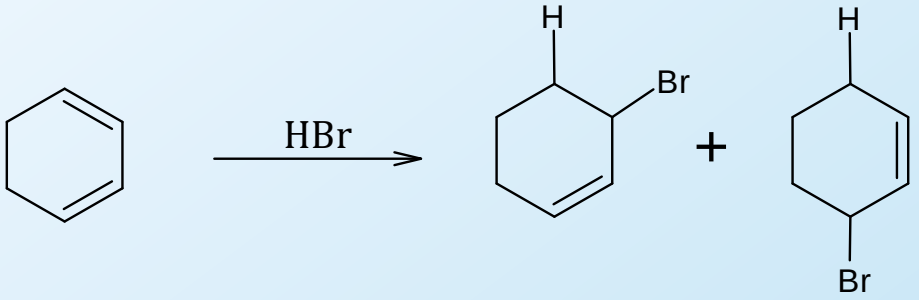
The two products, 1,2- and 1,4 addition are called the kinetic and thermodynamic respectively. Kinetic product is the fast forming product and can form at low temperature and is more stable at low temperature. The 1,4-thermodynamic product is formed after resonance and at a higher temperature. This is the more stable product.

Addition in Cyclic Compounds

Cyclic dienes will also give 1,2 and 1,4 products.



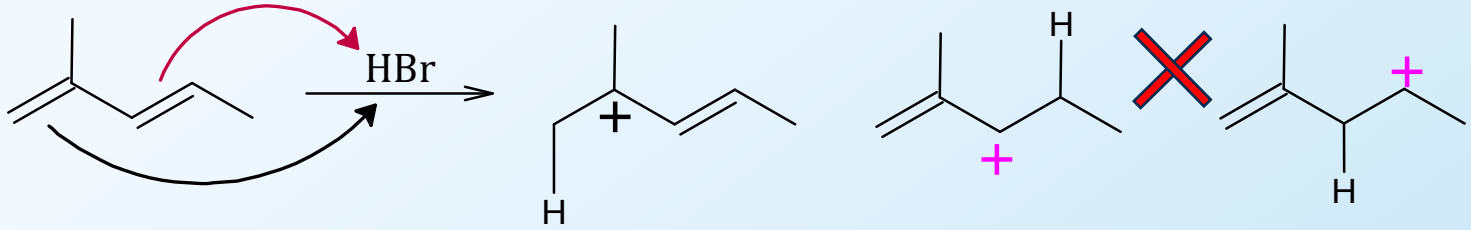
One has to be careful with cyclic compounds, because in some cases the 1,2 and 1,4 addition products are identical, as shown below.



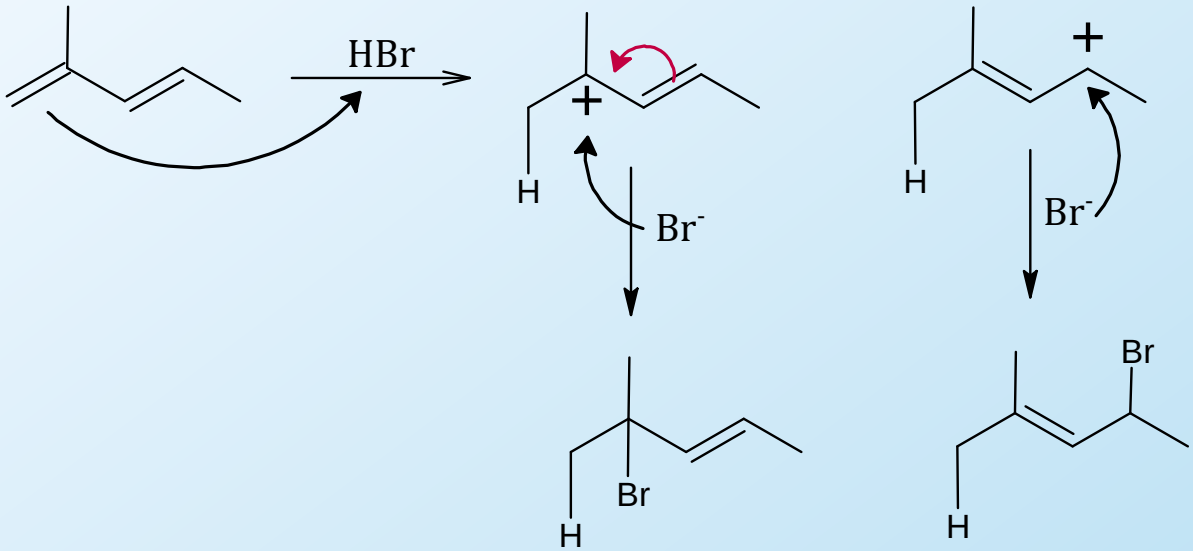
It might seem that there are two products but once you name them, 3-bromocyclohexene, we know they are the same ☺.

Addition with Substitution on Dienes

When there is a substitution on the diene then the more stable carbocation will form, as shown below. The carbocation on the right is not going to form as the first one is 3° while the second one is 2° carbocation..



The 1,2 and 1,4 products will form only from the first intermediate.



Key Concepts

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