Reactions of Dienes

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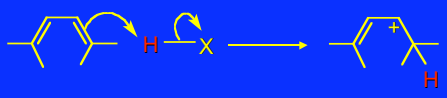
isolated dienes: double bonds react independently of one another

conjugated dienes: reactivity pattern requires us to think of conjugated diene system as a functional group of its own

Addition of Hydrogen Halides to Conjugated Dienes

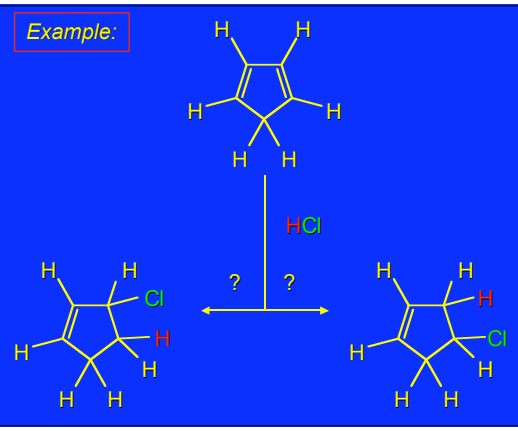
Electrophilic Addition to Conjugated Dienes



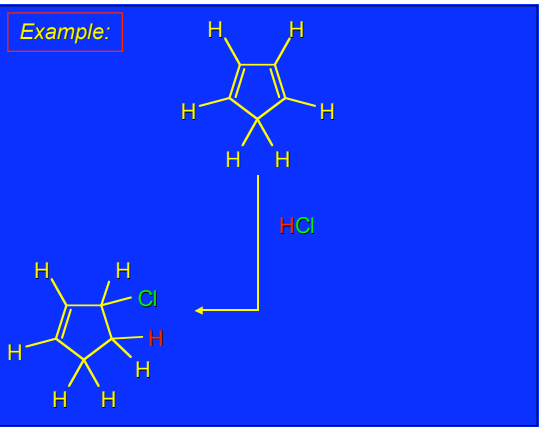
Proton adds to end of diene system

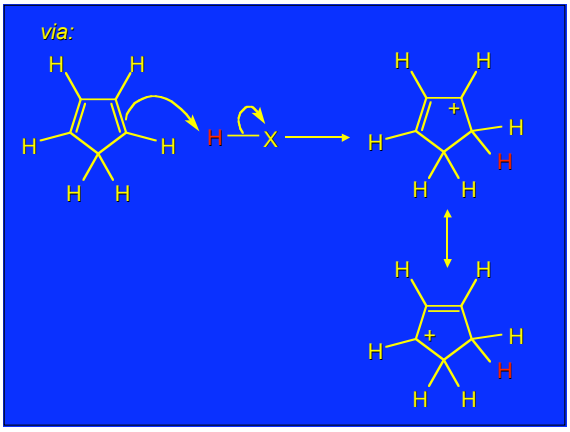
Carbocation formed is allylic

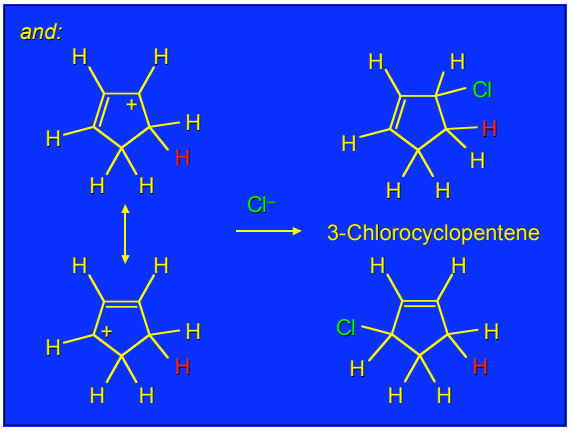
Example:

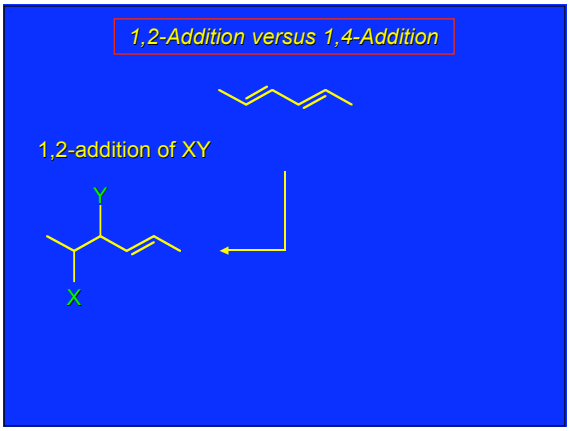


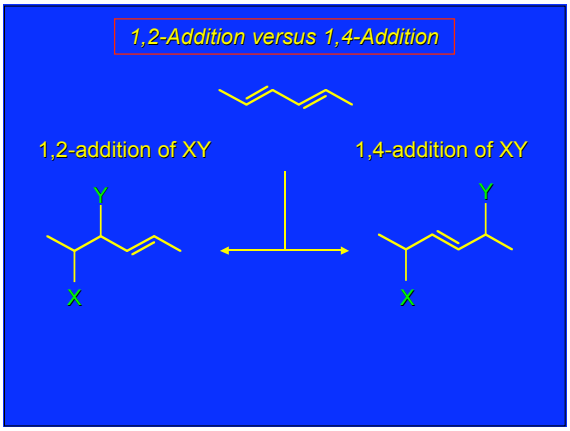
Example:

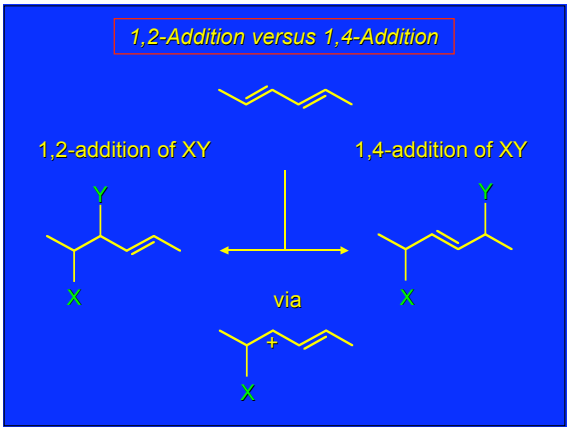


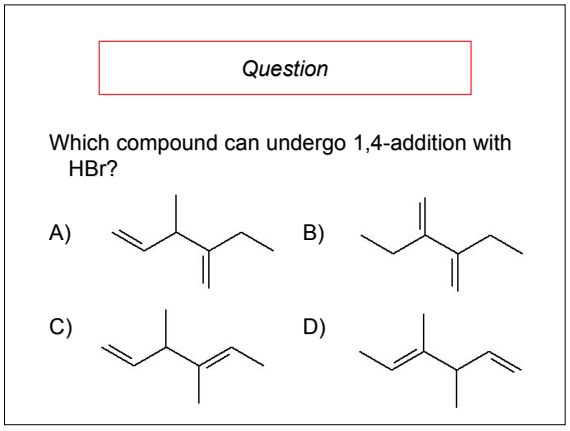

via:
H
X


and:
Cl⁻
3-Chlorocyclopentene
Cl
H

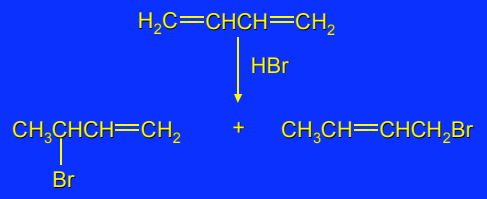

1,2-Addition versus 1,4-Addition
1,2-addition of XY
Y
X


1,2-Addition versus 1,4-Addition
1,2-addition of XY
1,4-addition of XY
Y
X


1,2-Addition versus 1,4-Addition
1,2-addition of XY
1,4-addition of XY
Y
X
via
+


Question
Which compound can undergo 1,4-addition with HBr?
A)
B)
C)
D)

HBr Addition to 1,3-Butadiene



electrophilic addition

1,2 and 1,4-addition both observed

product ratio depends on temperature

Rationale

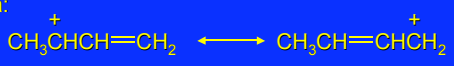
3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.

formed faster

Rationale

3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.

via:



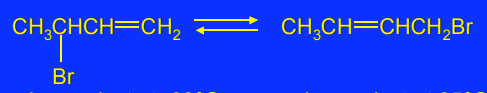
Rationale

1-Bromo-2-butene is more stable than 3-bromo-1-butene because it has a more highly substituted double bond.

more stable

Rationale

The two products equilibrate at 25°C. Once equilibrium is established, the more stable isomer predominates.

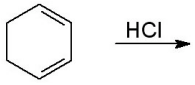


major product at -80°C (formed faster)

major product at 25°C (more stable)

Question

How many different products will be isolated from the reaction of 1,3-cyclohexadiene with HCl?

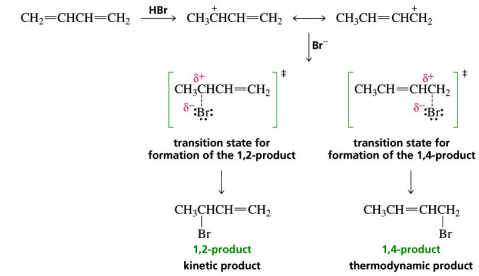


A) one
B) two
C) three
D) four

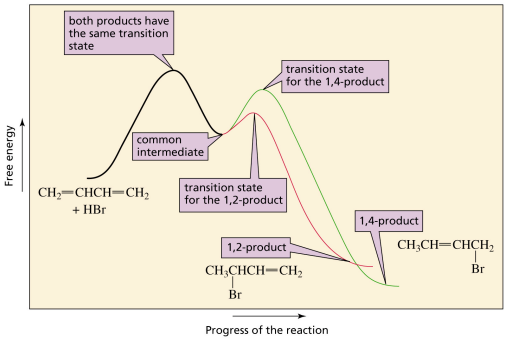
Kinetic Control versus Thermodynamic Control

Kinetic control: major product is the one formed at the fastest rate

Thermodynamic control: major product is the one that is the most stable



Consider the reaction coordinate diagram …

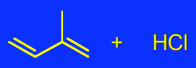


Problem

Addition of hydrogen chloride to 2-methyl-1,3-butadiene is a kinetically controlled reaction and gives one product in much greater amounts than any isomers. What is this product?

Problem

Think mechanistically.



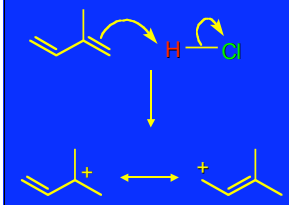
Protonation occurs:

- at end of diene system
- in direction that gives most stable carbocation

Kinetically controlled product corresponds to attack by chloride ion at carbon that has the greatest share of positive charge in the carbocation

Problem

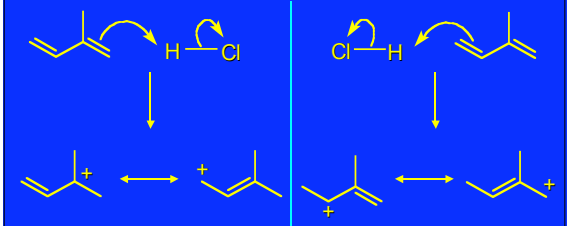
Think mechanistically



one resonance form is tertiary carbocation; other is primary

Problem

Think mechanistically

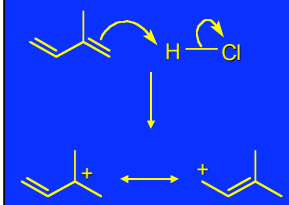


one resonance form is tertiary carbocation; other is primary

one resonance form is secondary carbocation; other is primary

Problem

Think mechanistically



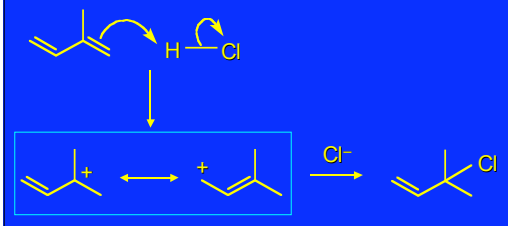
one resonance form is tertiary carbocation; other is primary

More stable carbocation

Is attacked by chloride ion at carbon that bears greater share of positive charge

Problem

Think mechanistically



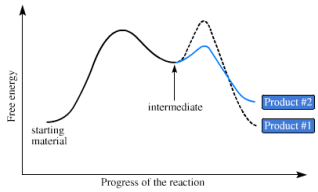
one resonance form is tertiary carbocation; other is primary

major product

The 1,4-addition product is NOT always the thermodynamic product …

Always compare the intermediates and products to assign the kinetic (PATHWAY) and the thermodynamic product (Lower ENERGY STATE)

Click "Product #1" or "Product #2" to label the KINETIC product.

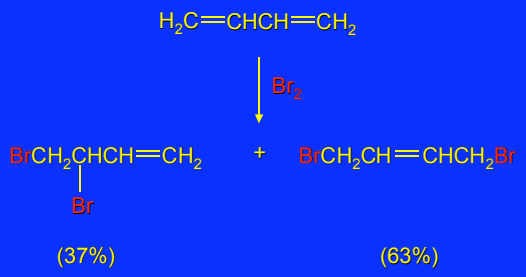


Example 1

Halogen Addition to Dienes

gives mixtures of 1,2 and 1,4-addition products

Example



Question

How many different possible products (not considering stereoisomers), can be formed from the reaction of 1,3-dimethyl-1,3-cyclohexadiene with Br_2?

A) one
B) two
C) three
D) four