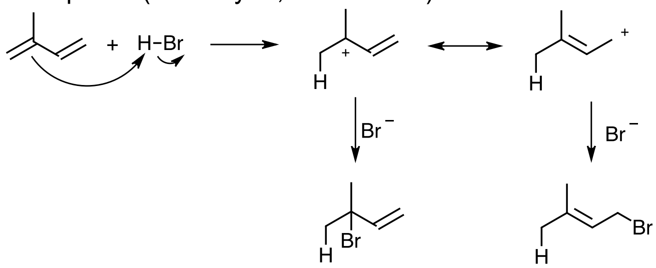
Objective 5. Identify a conjugated diene and understand electrophilic addition reactions of dienes.

1. A typical C-C single bond length is 153 pm and C=C bond length is 134 pm. In 1,3-butadiene, the C2-C3 single bond is 148 pm.
a. This experimental observation suggests the pi electrons in the two pi bonds are _____.
b. Would you expect the C=C bond length in 1,3-butadiene to be longer or shorter that 134 pm. Give reasons.
c. Pi bonds are nucleophiles. Explain why the pi bond in 1,3-butadiene is a weaker nucleophile than a simple pi bond.
d. Draw a resonance structure of 1,3-butadiene. Which resonance structure is the major contributor?

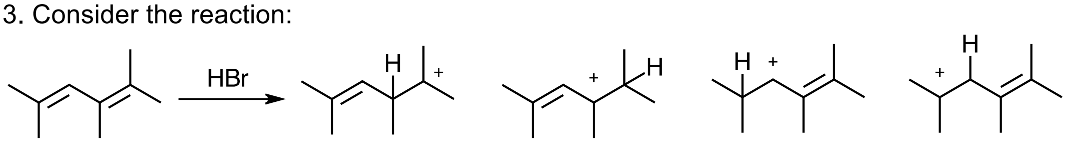
2. Isoprene (2-methyl-1,3-butadiene) reacts with HBr in an addition reaction to form at least two products.



1,2 product   1,4 product

a. See the reactants. Circle the nucleophilic bond. Box the electrophilic atom.
b. See the carbocation intermediate. Use curved arrows to go from one resonance structure to the other.
c. Use curved arrows to show how Br^- reacts with each resonance structure to form the 1,2 product and 1,4 product.
d. Use curved arrows to show how the pi bond between C3 and C4 reacts with HBr. Draw resonance structures of the intermediates. Then, use curved arrows to show how Br^- reacts with each resonance structure to form products. Note: you will get different products than the 1,2 and 1,4 products shown above.

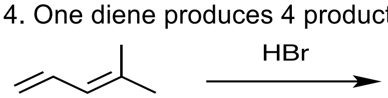
3. Consider the reaction:

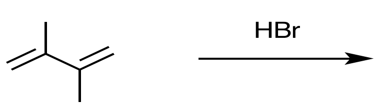


A   B   C   D

a. Use curved arrows to show how each intermediate forms.
b. Intermediates B and C are allylic carbocations. Draw resonance structures for Intermediates B and C.
c. Which intermediate is the most stable? Give reasons.
d. Draw the structures of the 1,2 product and 1,4 product. Note: there are 2 sets of the 1,2 and 1,4 products.

4. One diene produces 4 products whereas the other diene produces 2. Explain.





5. Klein, Problem 17.35. Identify the structure of the conjugated diene that will react with one equivalent of HBr to yield a racemic mixture of 3-bromocyclohexene.

Thermodynamic vs. kinetic control.
6. In Question 2,

a. explain why the carbocation intermediate on the left is more stable than the carbocation intermediate on the right. (kinetic control)
b. Explain why the alkene product on the right is more stable than the alkene product on the left. (thermodynamic control)
c. Draw a reaction energy diagram that shows the relative energies of the carbocation intermediates and alkene products. Explain why the less stable carbocation forms the more stable alkene product at high temperature.

7. In Question 3,
a. (i) draw the resonance structure of allylic carbocation B. Which carbocation resonance structure is more stable? Which carbocation forms at low temperature?
(ii) Draw the structure of the alkene that forms from each carbocation. Which alkene forms at low temperature?
b. (i) Draw the resonance structure of allylic carbocation C. Which carbocation resonance structure is more stable? Which carbocation forms at low temperature?
(ii) Draw the structure of the alkene that forms from each carbocation. Which alkene forms at low temperature?

8. In Question 4, the second reaction forms two products. Which product forms at high temperature? Draw the structure of the allylic carbocation and resonance structure. Identify the less stable carbocation.