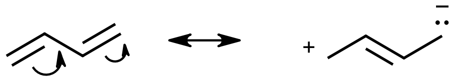
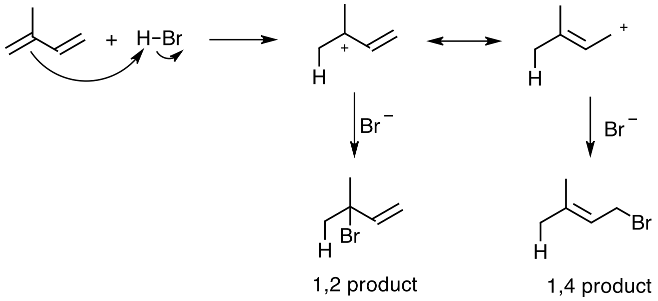
Objective 5 Quiz Practice Problems Solutions

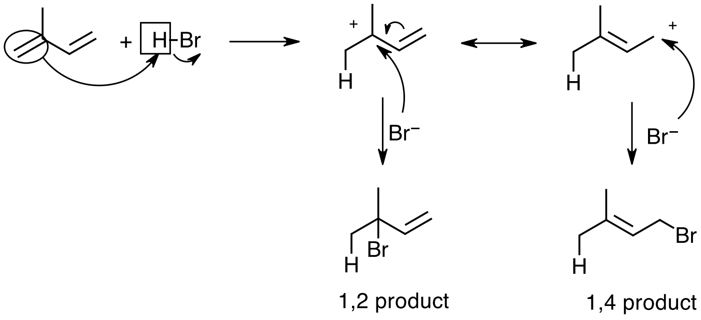
1. A typical C-C single bond length is 153 pm and C=C bond length is 134 pm. In 1,3-butadiene, the C2-C3 single bond is 148 pm.
a. This experimental observation suggests the pi electrons in the two pi bonds are ______.
b. Would you expect the C=C bond length in 1,3-butadiene to be longer or shorter than 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?
Answer:
a. delocalized
b. C=C bond length in 1,3-butadiene is longer tham 134 pm
c. Delocalized pi electrons are more spread out.
d. The left structure is the major contributor. It is more stable based on formal charge rules.



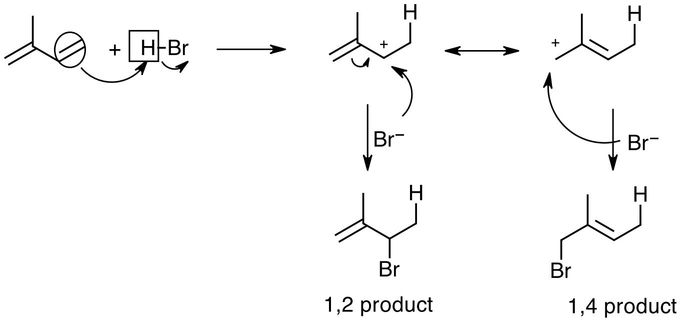
2. Isoprene (2-methyl-1,3-butadiene) reacts with HBr in an addition reaction to form at least two products.



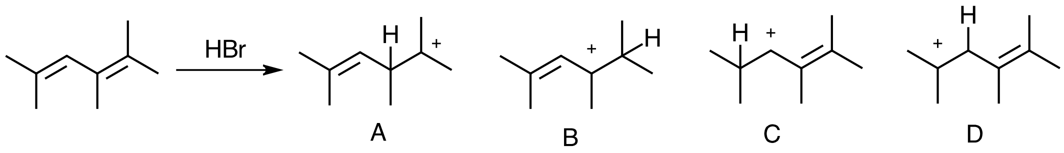
a. See the reactants. Circle the nucleophilic bond. Box the electrophilic atom.
b. See the carbocation intermediate. Use curved arrows to go from one resonance structure to the other.
c. Use curved arrows to show how Br$^-$ reacts with each resonance structure to form the 1,2 product and 1,4 product.
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.
Answer:
a-c.



d.



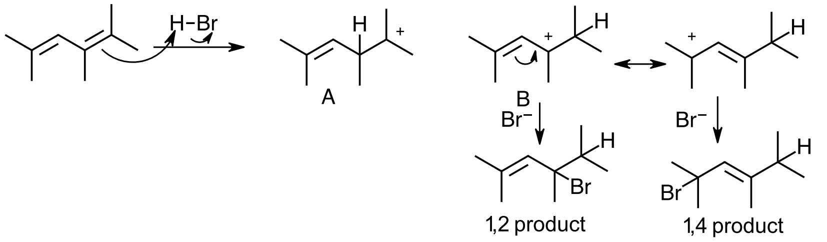
3. Consider the reaction:

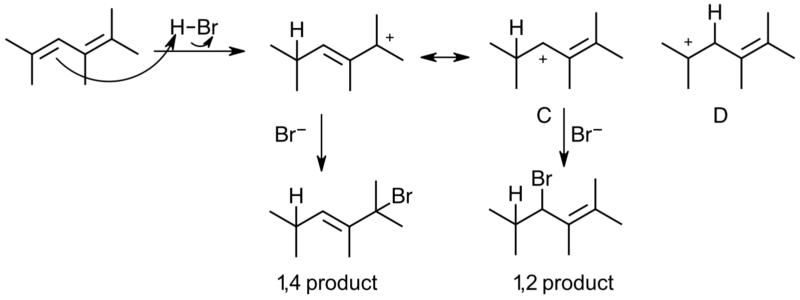


a. Use curved arrows to show how each intermediate forms.
b. Intermediates B and C are allylic carbocations. Draw resonance structures for Intermediates B and C.
c. Which intermediate is the most stable? Give reasons.
d. Draw the structures of the 1,2 product and 1,4 product. Note: there are 2 sets of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

Answer:

a and b.

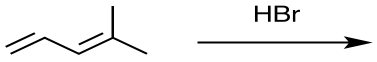


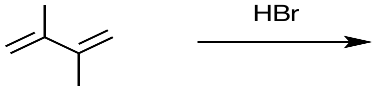


c. A and D are 3^{o} carbocations but B and C are 3^{o} allylic carbocations ==> most stable.

d. B and C and their resonance structures form the 1,2 products and 1,4 products.

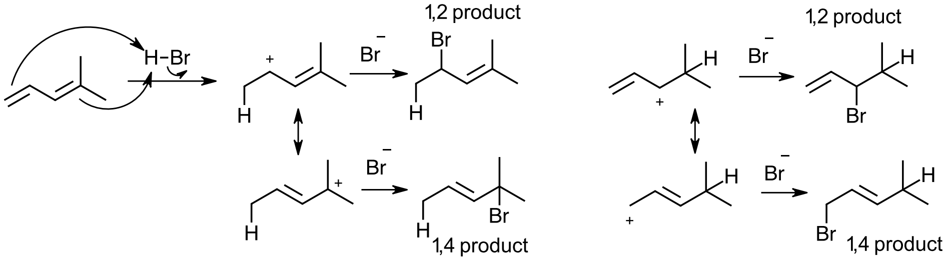
4. One diene produces 4 products whereas the other diene produces 2. Explain.



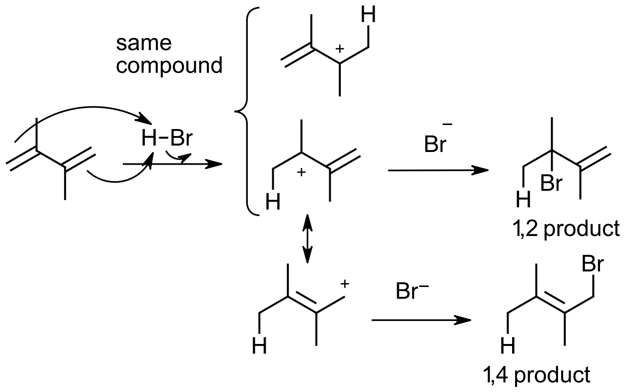


Answer:

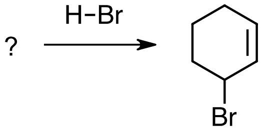
2-methyl-2,4-pentadiene produces 4 products.



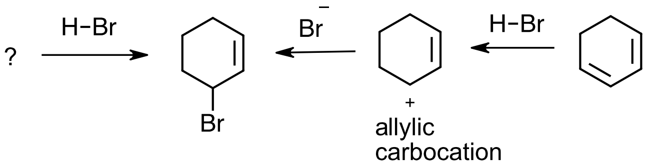
2,3-dimethyl-1,3-butadiene is a symmetrical diene. The same carbocation intermediate forms when HBr reacts at each C=C bond.



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.

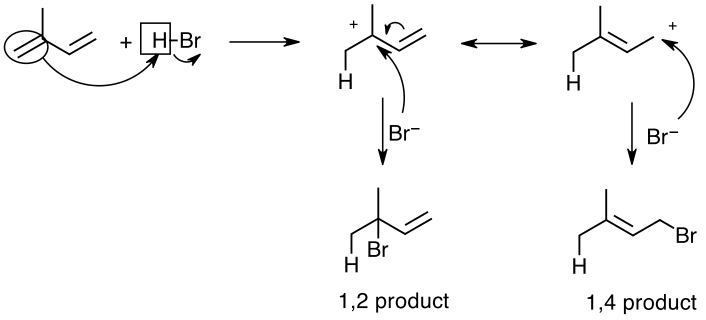


Answer: work backwards.

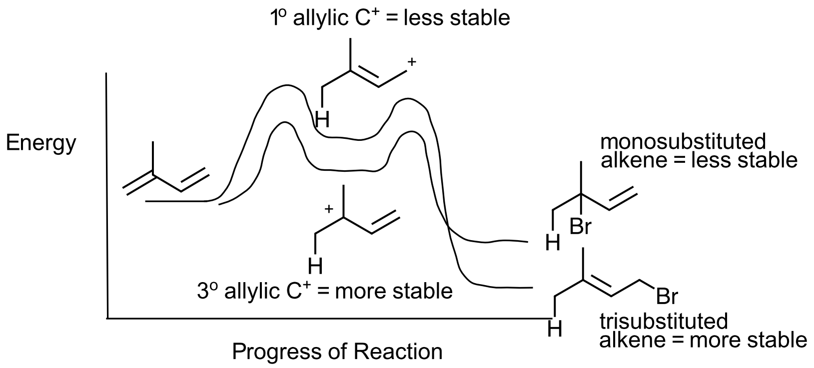


1,3-cyclohexadiene is the conjugated diene.
The carbon bonded to Br is a chirality center. Racemic mixture because Br- can react on either side (top or bottom) of trigonal planar carbocation.

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.
Answers:
a. The 3^{o} allylic carbocation intermediate on the left is more stable than the 1^{o} allylic carbocation intermediate on the right. The more stable 3^{o} allylic carbocation intermediate forms faster than the less stable 1^{o} allylic carbocation intermediate.

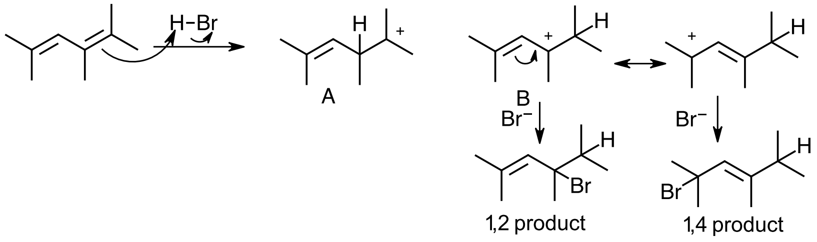


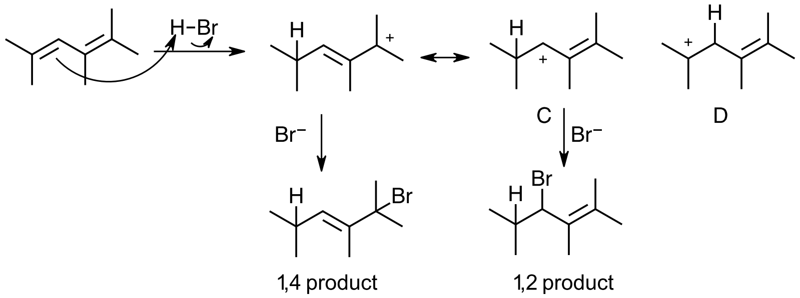
b. The trisubsituted alkene product on the right is more stable than the monosubsituted alkene product on the left.
c. Reaction energy diagram:



The reaction of 2-methyl-1,3-butadiene + HBr to form each carbocation intermediate has separate activation energies. The reaction of 2-methyl-1,3-butadiene + HBr to form the higher energy, less stable 1^{o} allylic carbocation has a higher activation energy and occurs SLOWER than the reaction of 2-methyl-1,3-butadiene + HBr to form the lower energy, more stable 3^{o} allylic carbocation, which has a lower activation energy and occurs FASTER.
At high temperature, there is enough energy to overcome the higher activation energy to form the higher energy, less stable 1^{o} allylic carbocation. This less stable carbocation reacts with Br^{-} to form the more stable trisubstituted alkene product. So at high T, the major product will be the more stable trisubstituted alkene product.

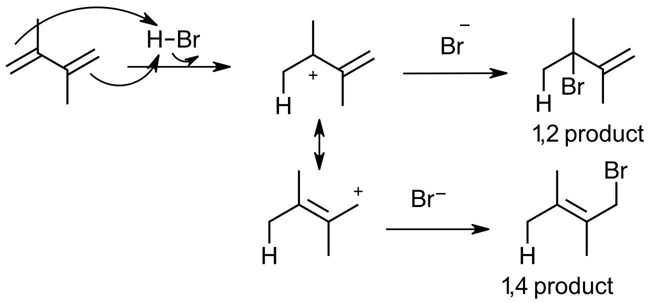
7. In Question 3,
a. (i) draw the resonance structure of allylic carbocation B. Which carbocation resonance structure is more stable? Which carbocation forms at low temperature?
(ii) Draw the structure of the alkene that forms from each carbocation. Which alkene forms at low temperature?
b. (i) Draw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





a. (i) Carbocation intermediate B and its resonance structure are 3^{o} allylic carbocations and have the same stability. Both form at low T.
(ii) The alkene that forms at low T comes from the more stable carbocation intermediate. Both alkenes are trisubstituted alkenes and have the same stability. So both form at low T.
b. (i) Carbocation intermediate C is a 2^{o} allylic carbocation and its resonance structure is a 3^{o} allylic carbocation. The 3^{o} allylic carbocation is more stable and forms at low T (kinetic control).
(ii) The alkene that forms at low T comes from the more stable carbocation intermediate. The 3^{o} allylic carbocation is more stable and forms at low T so the 1,4 alkene product (disubstituted and less stable) forms at low T.

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.
Answer:



The 3° allylic carbocation intermediate on the top is more stable than the 1° allylic carbocation intermediate on the bottom. The more stable 3° allylic carbocation intermediate forms faster and at low T (kinetic control).

The less stable 1° allylic carbocation intermediate forms slower and at high T (need enough energy to overcome the higher activation energy) so the product that forms at high T is the more stable, trisubstituted 1,4 product (thermodynamic control).