

CFQ & PP: Addition to Carbon-Carbon π Bonds

Reading

Brown and Foote: Chapters 5, 6 and 10

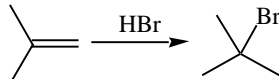
Suggested Text Exercises

Brown and Foote:

- Chapter 5: 7 - 12, 16 - 19, 21, 23 - 35
- Chapter 6: all
- Chapter 10: 3 - 5, 9 - 20, 23 - 26

Concept Focus Questions

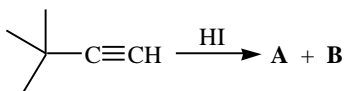
1. Provide a clear but concise definition for each term.
 - a. Addition reaction
 - b. Anti addition
 - c. Anti-Markovnikov orientation
 - d. Cycloaddition
 - e. Markovnikov orientation
 - f. Regioselective reaction
 - g. Syn addition
 - h. Tautomers
2. In addition reactions of C-C π bonds, what is the nucleophile and why? Show a generic mechanism for this type of reaction. Describe the mechanism in your own words.
3. In your own words, describe the kinetics of the above reaction for each step in the mechanism. How are the kinetics similar to the kinetics of the S_N1 reaction? How are they different? What is the rate-limiting step?

4. Consider the reaction of an alkene with HBr: 

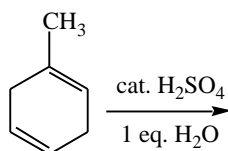
a. Write the mechanism for the reaction.

b. Why do the π bond electrons attack the hydrogen end of HBr?

c. Briefly explain why the addition of HBr gives the product shown instead of the primary alkyl halide.
5. State Markovnikov's Rule. Briefly explain the underlying mechanistic factor controlling Markovnikov's Rule.
6. Should an alkyne react with HBr in the same manner as an alkene? Briefly explain why or why not.
7. Give the structures of products **A** and **B**. Write the mechanism for the formation of each.



8. Consider the reaction of a nonconjugated diene with aqueous sulfuric acid:



- Show the major product for the following reaction and provide a detailed mechanism for the reaction.
- Show the product if a second equivalent of H₂O is added.
- What happens if no acid catalyst is added?

Concept Focus Questions Solutions

- Addition reaction:** A reaction in which the products consist of most or all of the atoms of the reactants.

Anti addition: An addition reaction in which fragments of one reactant are added to the opposite faces of the other reactant.

Anti-Markovnikov orientation: An addition reaction of an alkene or alkyne with a generic electrophile H-X in which the hydrogen atom of H-X becomes bonded to the end of the bond that bears the least number of hydrogen atoms to begin with.

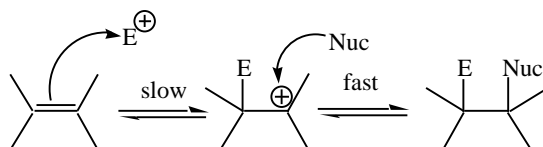
Cycloaddition: An addition reaction resulting in a new ring.

Markovnikov orientation: An addition reaction of an alkene or alkyne with a generic electrophile H-X in which the hydrogen atom of H-X becomes bonded to the end of the bond that bears the most number of hydrogen atoms to begin with.

Regioselective reaction: A reaction that produces only one of several possible constitutional isomers as the only product.

Syn addition: An addition reaction in which fragments of one reactant are added to the same face of the other reactant.

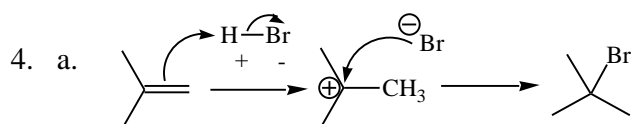
Tautomers: Constitutional isomers that are conceptually related by the shift of a hydrogen atom and one or more bonds.
- The nucleophile is the molecule that contains the bond in the first step because it is the source of electrons and the species that attacks the carbocation in the second step.



Mechanism description: The bond of an alkene or alkyne is a source of readily available electrons, and thus makes these functional groups nucleophilic. Attack of an electrophile on the bond results in a new bond between the electrophile and one end of what was the bond. The other carbon of the bond, having lost a pair of electrons, now bears a positive charge (a carbocation). The carbocation reacts so as to fill its open octet by capturing a nucleophile. The net effect is the replacement of

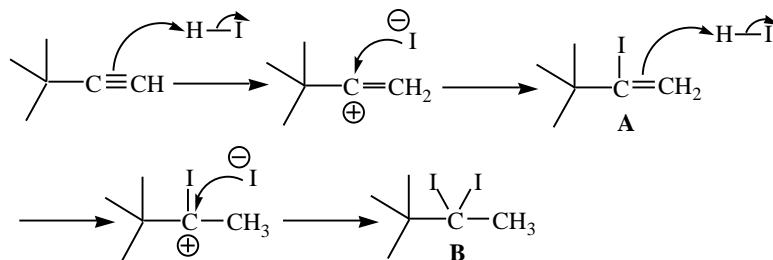
the portion of the double or triple bond with two new bonds, an process that is generally assumed to be exothermic as most bonds are weaker than the corresponding bonds.

3. Addition to a C-C bond of an alkene or alkyne is a two step process. The first step breaks the bond and creates a carbocation. In the second step the carbocation accepts a nucleophile and a new bond results. This is energetically favorable and is the fast step. The kinetics of the reaction are similar to those of an S_N1 reaction in that the formation of an unfavorable, energetically expensive carbocation is the first and the rate determining step. It differs from an S_N1 reaction, however, in that the rate is not solely dependent on the concentration of one species, but instead is bimolecular.

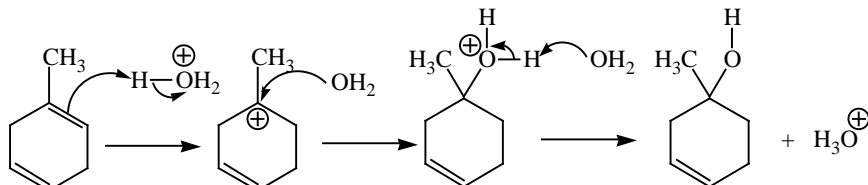


- b. The hydrogen was attacked because it is less electronegative than bromine and bears the + in the HBr bond.
- c. In looking at the mechanism in 3a, we can see that the formation of the carbocation is the first step. The formation of a more stable carbocation has a lower energy of activation (E_{act}). A tertiary carbocation is much more stable than an isomeric primary carbocation, so the E_{act} for the formation of the tertiary carbocation is lower than the E_{act} for the formation of the primary carbocation.
5. Markovnikov's Rule can be stated as: "In the addition of a hydrogen halide to an alkene, hydrogen adds to the carbon of the double bond having the greater number of hydrogens." The underlying mechanistic factor controlling Markovnikov's Rule is that the most stable carbocation intermediate is formed predominantly, leading to addition of the halide to the more alkyl substituted carbon. (Markovnikov only studied the reaction of HBr and HCl with alkenes, and formulated his rule based upon those observations. To be historically accurate, we should discuss Markovnikov's Rule on for these reactions. However in modern usage we apply to the rule just about any electrophilic addition to a C-C bond (alkene or alkyne) in which a new C-H bond is formed.)
6. We predict that an alkyne will react in the same manner as an alkene in the presence of HBr because the only difference is that an alkyne has two C-C bonds instead of just the one. This is another example of the concept that similar functional groups have similar reactions and reactivity.

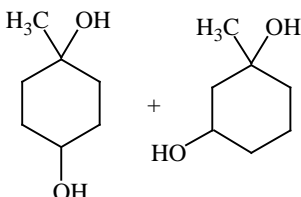
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8. a.



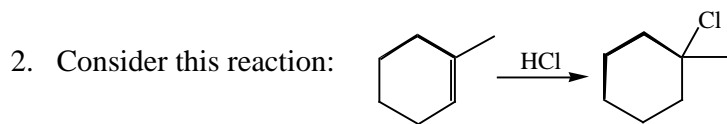
b.



- c. Water by itself is a poor electrophile, as the magnitude of δ^+ charge on the hydrogen atoms is not great enough for the reaction to proceed. Protonation of the water oxygen makes this oxygen atom more electron poor, thus amplifying the magnitude of the δ^+ on hydrogen. Hydronium ion is sufficiently electrophilic to undergo the energetically expensive reaction with the alkene π bond to form a carbocation. In the absence of acid catalyst, the reaction does not proceed at a useful rate.

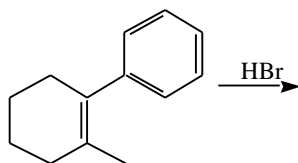
Practice Problems

1. Briefly explain why alkenes react with electrophiles but do not react with nucleophiles. Give an example that clearly illustrates your answer.

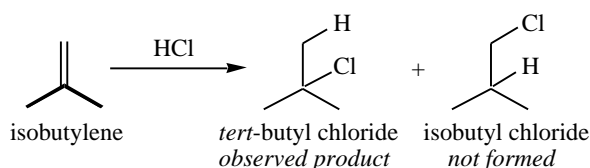


- Write the mechanism for this reaction.
 - Draw the transition state for the rate-determining step for this reaction.
 - Briefly explain your choice for the rate-determining step.
 - Write a reaction that is clearly faster than the reaction shown above.
 - Briefly explain why this reaction is faster.
3. Give an example of a regioselective reaction.

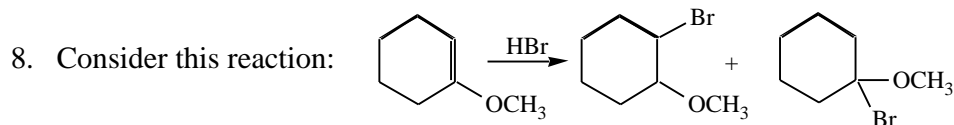
4. Consider this reaction:



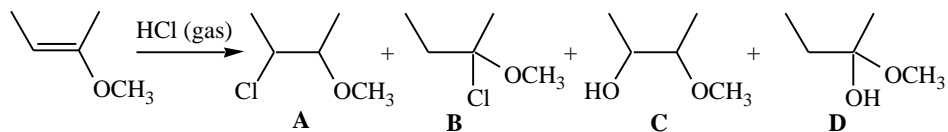
- Write a detailed curved-arrow mechanism that shows how the major product is formed.
 - Briefly explain why this isomer, instead of others, is formed.
5. According to Markovnikov's rule, isobutylene reacts with HCl to form *tert*-butyl chloride. No isobutyl chloride is formed in this reaction. Explain in detail why this is so.



6. State Markovnikov's rule. Write a reaction with complete mechanism that clearly illustrates Markovnikov's rule. Briefly explain the mechanistic origin of Markovnikov's rule.
7. Give a reaction that clearly illustrates anti-Markovnikov addition.

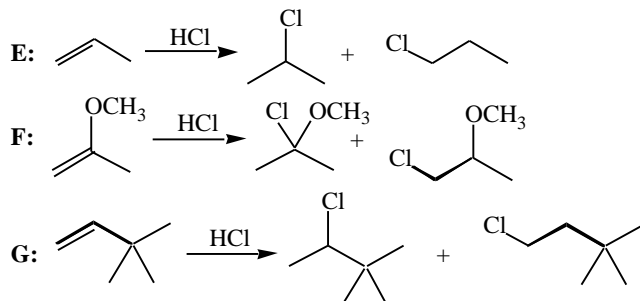


- Provide a complete curved-arrow mechanism that shows how the major product is formed.
 - Briefly explain your choice of major product.
9. Consider this reaction:



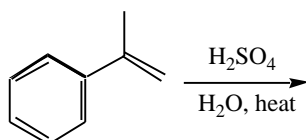
- Which is the major product of this reaction?
- Write a detailed mechanism that shows how the major product is formed.
- Clearly explain your choice of major product.
- Write a reaction that is similar to the one shown above, but obviously occurs at a faster rate. Explain your reasoning.

10. Consider reactions **E - G**:

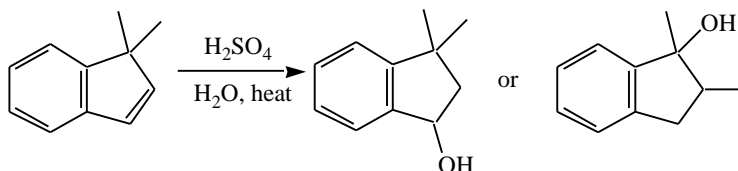


- Which reaction is the fastest? Briefly explain.
- What is the major product of the fastest reaction? Briefly explain.
- Write a detailed curved-arrow mechanism that shows how the major product is formed. Write "rds" above the arrow in the rate-determining step of your mechanism.
- Offer an explanation for your choice of rate-determining step.

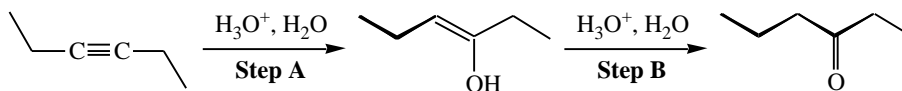
11. Consider this reaction:



- Provide a detailed, curved-arrow mechanism for the major product of this reaction.
 - Briefly explain why you chose this isomer to be the major product.
12. Draw a complete curved-arrow mechanism that shows how the major product is formed in the reaction shown below. Briefly explain your choice of major product.

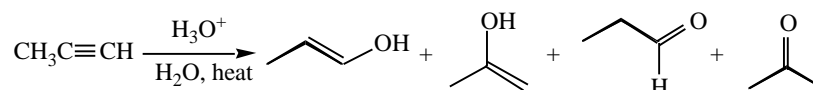


13. Why are the reactions of alkenes and alkynes so very similar? Write a pair of reactions that clearly illustrates this concept.
14. List two significant similarities between alkenes and alkynes. Clearly illustrate each similarity with a drawing or reaction.
15. List two significant differences between alkenes and alkynes. Clearly illustrate each difference with a drawing or reaction.
16. Consider this reaction:



- Provide a curved arrow mechanism both steps.
- Which step is faster? Briefly explain.

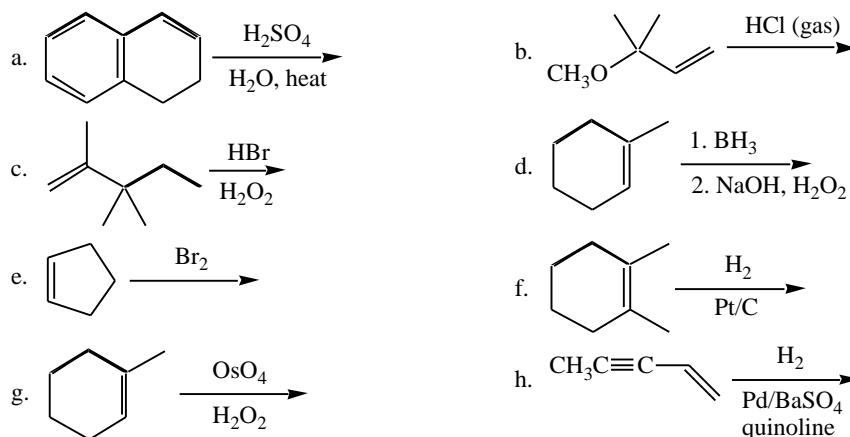
17. Draw a complete curved-arrow mechanism that shows how the major product is formed in this reaction.

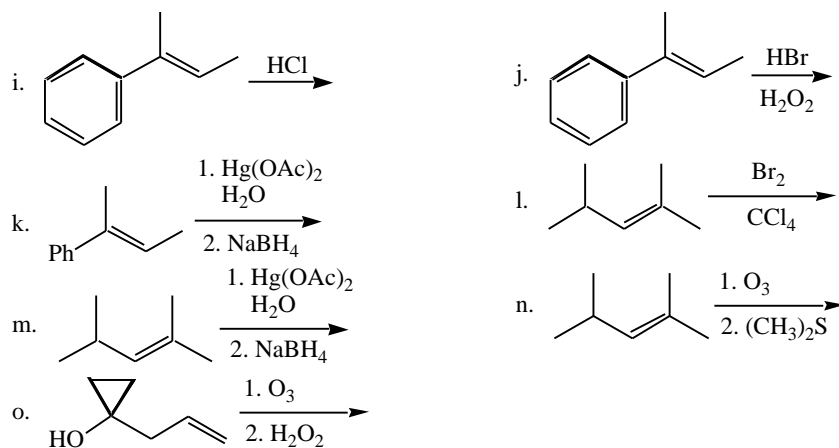


18. Briefly explain why BH_3 and $\text{Hg}(\text{OAc})_2$ are electrophiles.
19. For each reactant below, categorize its reaction with a C-C bond as "electrophilic addition" or "other." Write the reaction of each reactant with isobutylene, and any other reagents commonly used or needed with that reactant.

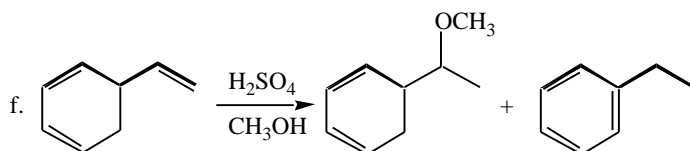
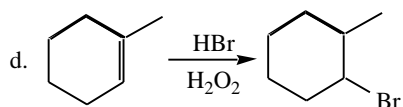
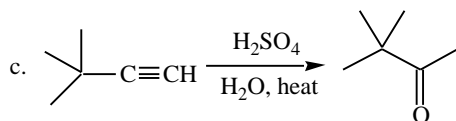
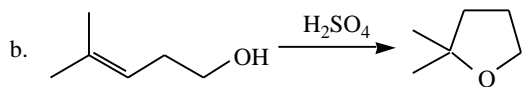
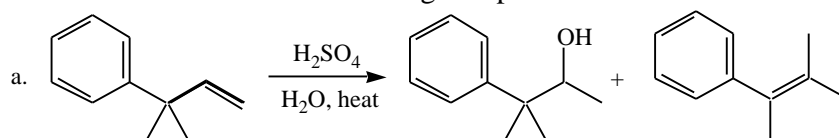
Reactant	Reaction Type	Reaction with Isobutylene
HBr (gas)		
H_3O^+		
BH_3		
H_2		
O_3		
OsO_4		
HBr/ H_2O_2		
Br_2		
$\text{Hg}(\text{OAc})_2$		

20. Provide the organic product(s) of the following reactions. If more than one product is formed, indicate which product (if any) is the major one. If no reaction occurs, write "NR." Pay careful attention to the stereochemistry of the reactants and products.

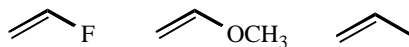




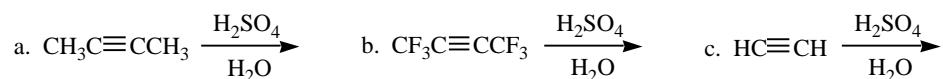
21. Write a detailed mechanism for the following reactions. Be sure that your mechanisms account for all of the given products.



22. Determine the alkenes that will react fastest and slowest in a typical electrophilic addition reaction. Briefly explain your answer.



23. Draw the product and mechanism for the fastest of the following reactions.

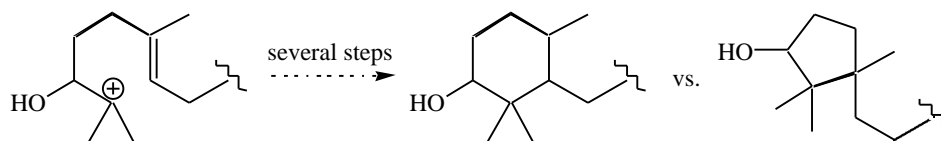


24. Give the structure of two stereoisomeric alkenes with molecular formula C_6H_{12} that will react with HI to give the same single product, and will undergo catalytic hydrogenation to give n-hexane.

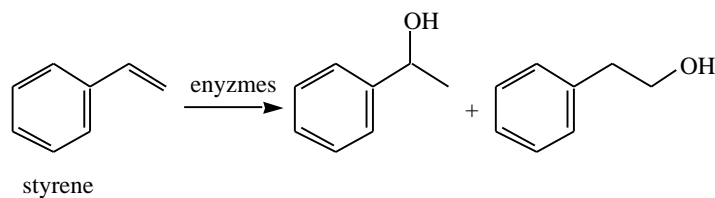
25. Carefully explain why the reaction of an alkene with HBr in the presence of peroxides gives a different product than the same reaction in the absence of peroxides. A mechanism can be used to justify your answer, but your mechanism must clearly show why these reaction conditions give different products.

26. The first mechanism step of the reactions of alkenes with OsO_4 and ozone are very similar. Briefly discuss why this is so. An illustration will be very useful.

27. An early step in the biosynthesis of steroids from squalene involves the reaction of a carbocation with an alkene to form the A ring of the steroid. This A ring is a cyclohexane, not a cyclopentane. Provide a rationale for this selectivity. Hint: Curved arrows will help clarify your answer.



28. The body disposes of foreign compounds by metabolism to form compounds that are more polar and more water soluble, thus more easily excreted.

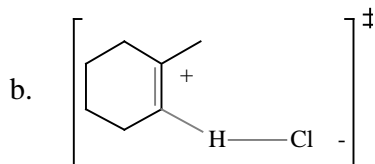
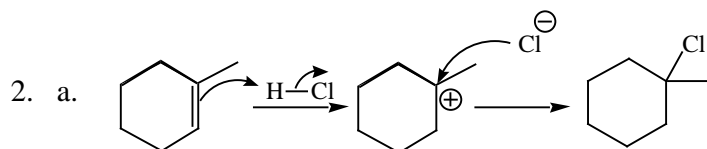
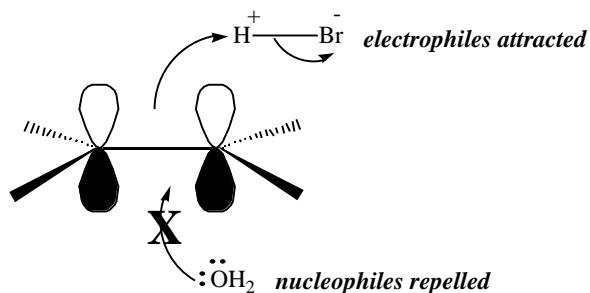


As a model for such a process, write major product of the reaction of styrene, a carcinogenic hydrocarbon, with H_3O^+ and H_2O . Include a mechanism to show how this major product is formed. Briefly explain your choice of major product for this reaction.

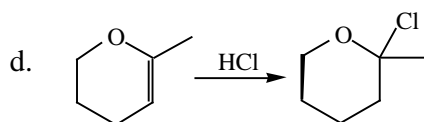
Practice Problems Solutions

- Alkenes have clouds of electron density above and below the plane of the double bond. Because unlike charges attract, this area of electron density will attract things with a partial or full positive charge (electrophiles such as hydrogen bromide). Like

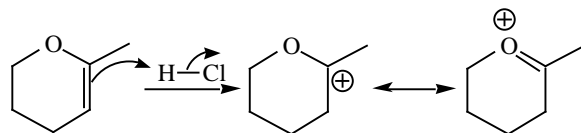
charges repel, so the electron cloud will repel things with a partial or full negative charge (nucleophiles such as water).



c. The rate-determining step (rds) is the mechanism step with the largest (most positive) energy of activation (E_{act}). In this HCl addition reaction, the first step is the rds because a carbocation is being formed; this is an energetically expensive process. The second step is much faster because it involves only bond making.

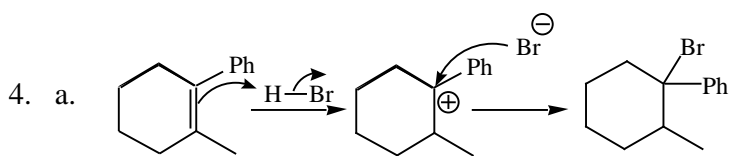


e. The rate of the reaction is controlled by the transition state for the rds. Stabilizing this transition state will lower the E_{act} and thus accelerate the reaction. In this example, replacing the methylene group (CH_2) with an oxygen atom adds resonance stabilization to the carbocation intermediate.



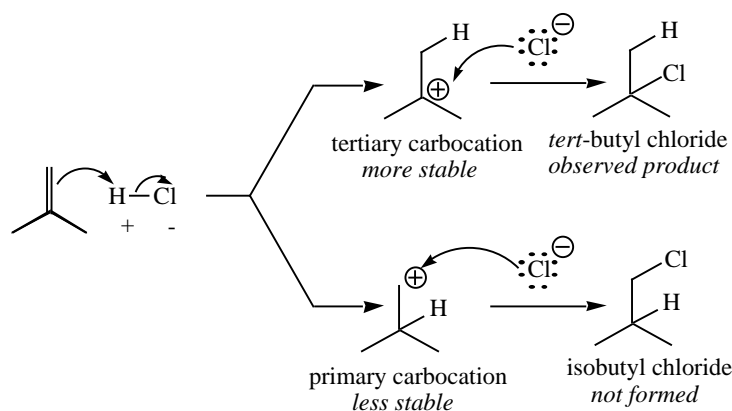
This stabilization results in a faster reaction.

3. A reaction is said to be regioselective if bond forming or bond breaking occurs at one atom or region of the molecule in preference to all other atoms or regions. An example of this is the electrophilic addition to C-C bonds of hydrogen halides, since the halide adds to the most alkyl-substituted carbon as the major product. In this example, the "region" is one end of the bond instead of the other.



- b. Addition of the HBr to the alkene bond proceeds through the most stable carbocation. In this case, the carbocation is tertiary and benzylic (which results in significant resonance stabilization). The other alkene-derived carbocation would also be tertiary, but would not enjoy resonance stabilization. Electrophilic attack on the benzene ring could lead to a tertiary carbocation with resonance. This would disrupt aromaticity, and is therefore energetically expensive. (Benzene aromaticity is 36 kcal/mole of stabilization.)

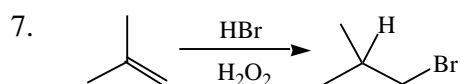
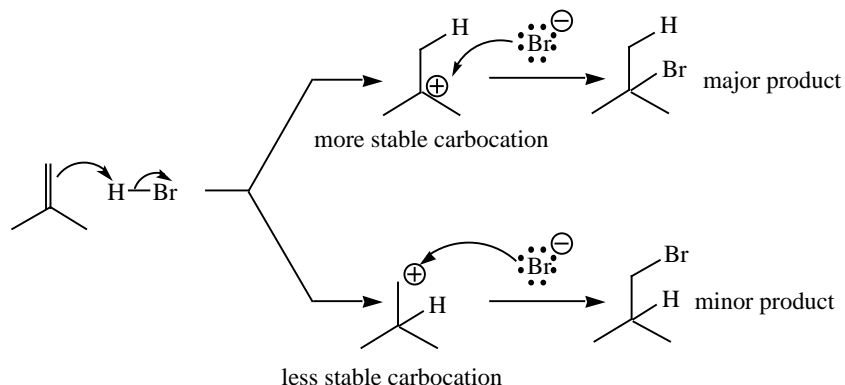
5. Electrophilic attack of HCl on the bond results in carbocation formation.



The most stable carbocation (tertiary in this case) forms more readily. This fact is the fundamental idea behind Markovnikov's rule. The less stable primary carbocation does not form to any significant extent. The tertiary carbocation captures chloride ion to form tert-butyl chloride, while the primary carbocation forms isobutyl chloride. Because no primary carbocation forms, no isobutyl chloride can result.

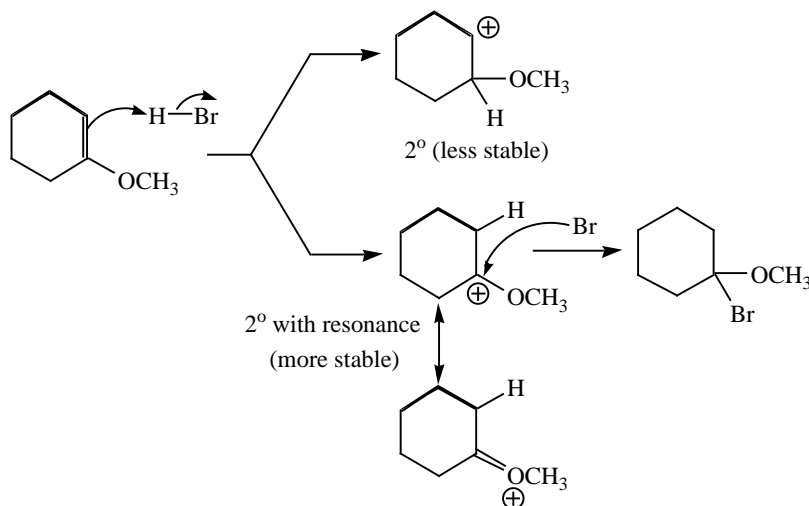
6. Markovnikov's rule: "When an alkene reacts with HBr, the hydrogen atom is added to the carbon atom which has the most number of hydrogen atoms already bonded to it." ("Them that has, gets.") Note: Markovnikov only studied the reactions of HBr, so to be completely accurate, Markovnikov's rule applies only to HBr additions. The hydrogen atom of HBr is added to the alkene so as to form the most stable

carbocation. This carbocation captures a nucleophile (Br^-), to give the more highly substituted alkyl bromide.



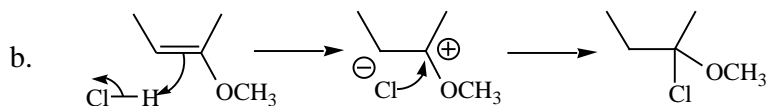
This reaction is anti-Markovnikov because the new hydrogen atom has become bonded to the alkene carbon that had the least number of hydrogen atoms to start with.

8. a. Mechanism:

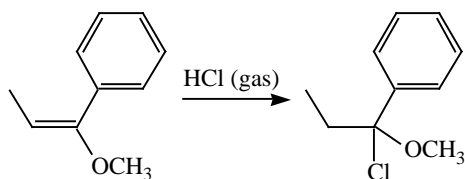


b. In any mechanism step that produces a reactive intermediate such as a carbocation, carbanion or radical, the more stable reactive intermediate is formed more readily (lower energy of activation). In this case, both carbocations are secondary, but because the one with resonance is more stable it is formed more readily. Reaction of this carbocation with bromide ion affords the -bromoether product.

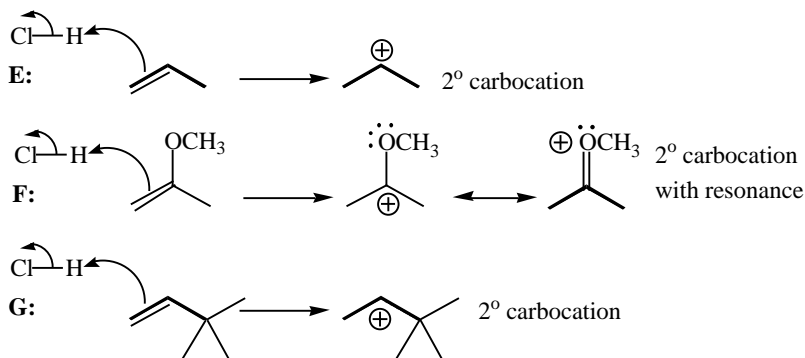
9. a. The major product of this reaction is **B**.



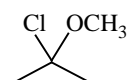
- c. Attack of the π bond on HCl will proceed to give the most stable carbocation. A secondary carbocation with resonance is more stable than a secondary carbocation without resonance. This fact controls the position of the chloride in the final product (regioselectivity). Products **C** and **D** cannot form because no water is present to be captured by the carbocation intermediate (note HCl gas, not aqueous HCl).
- d. The rate-determining step of this reaction is the formation of the carbocation. The more stable the carbocation, the faster the reaction. Thus, addition to afford a secondary carbocation with more resonance (provided by the benzene ring) will occur more quickly.

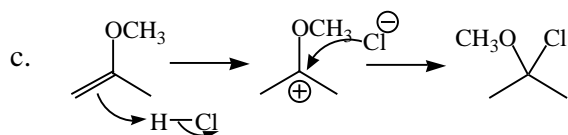


10. a. The relative rates of these reactions are controlled by their rate-determining steps (carbocation formation). The most stable carbocation is formed more quickly because its formation has a lower E_{act} .

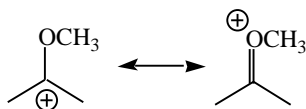


All the carbocations are secondary, but only the carbocation formed in reaction **F** has the extra stability afforded by resonance. Therefore the fastest reaction is **F**.

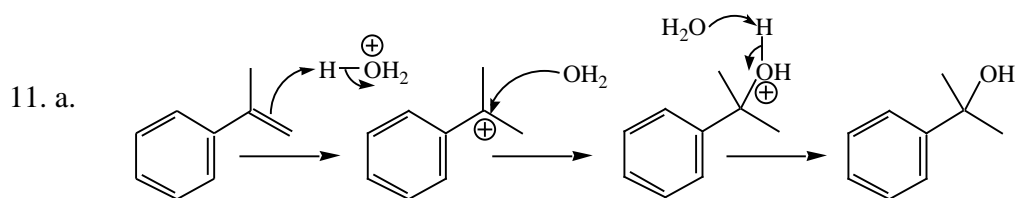
- b.  This product results from the capture of chloride ion by the carbocation intermediate, the formation of which is shown below.



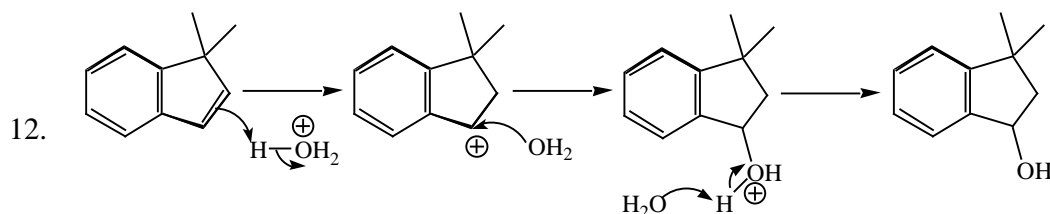
- d. When a reaction proceeds via a mechanism that has more than one step, the overall reaction rate is dominated by the rate-determining (slowest) step. In this reaction the slowest step is the first step in which the energetically expensive process of carbocation formation occurs. The more stable the carbocation that is formed, the faster the rate of this step. Of all the carbocations that would have to be formed to produce the products shown above, the most stable one (shown below) is secondary with resonance.



Because this carbocation is the most stable, it will be formed most quickly, and thus in the greatest amount. Because this is the most prevalent carbocation, it forms most of the product.



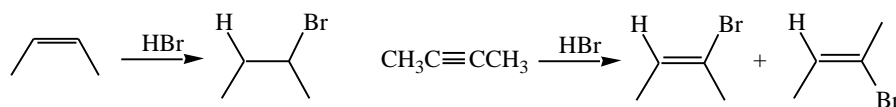
- b. Initial reaction of the alkene with H_3O^+ can form two carbocations. The more stable benzylic tertiary carbocation (shown in the mechanism above) is formed in preference to the less stable primary carbocation. This is the rate-determining step, and thus controls the product distribution. Formation of the more stable carbocation is the mechanistic basis for Markovnikov's rule.



Electrophilic addition to a π bond proceeds to give the most stable carbocation intermediate. Attack of the alkene on hydronium ion can yield two secondary carbocations, one of which has resonance stabilization. Formation of the secondary carbocation that has resonance leads to the secondary alcohol product shown above. Formation of the tertiary alcohol product would have to involve the less stable secondary carbocation, and would thus be disfavored.

13. The reactions of alkenes and alkynes are similar because they contain similar functional groups. Alkenes have a single carbon-carbon π bond, whereas alkynes have two carbon-carbon π bonds. These π bonds are sources of available electron density, so both alkenes and alkynes behave as nucleophiles. Both alkenes and alkynes can undergo addition reactions, in which the carbon-carbon π bond is

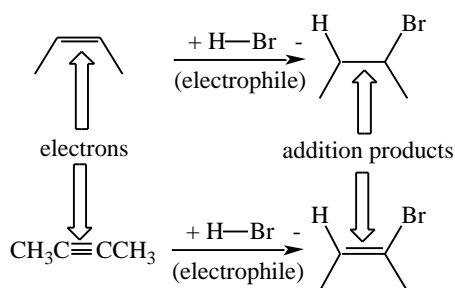
replaced by two new bonds. Such addition reactions are not all electrophilic. Illustrative example: Alkenes and alkynes both undergo electrophilic addition with HBr.



14. There are many possible acceptable answers to this question, as long as the answer gives a significant similarity. Some possibilities:

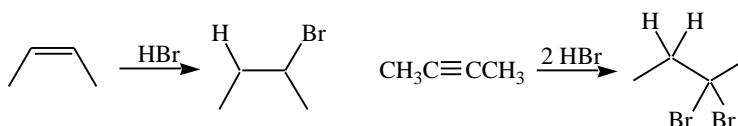
- The alkene and alkyne functional groups are both nucleophilic because they both have electrons to share with an electrophile.
- Alkenes and alkynes both undergo addition reactions.

The answer "alkenes and alkynes are similar because both begin with the letter "a" is not sufficiently significant. Both similarities can be illustrated by the same pair of reactions.

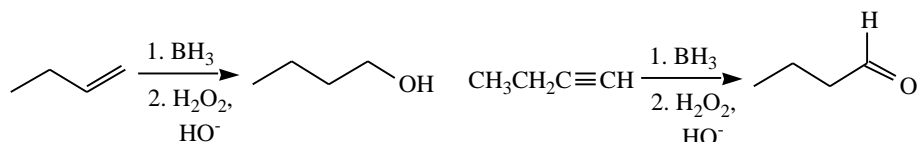


15. There are many possible acceptable answers to this question, as long as the answer gives a significant difference.

- One alkene molecule can react with one mole of HBr whereas an alkyne can react with two moles.

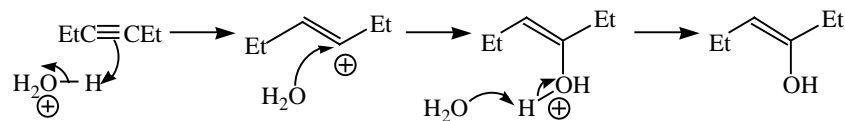


- Hydroboration of a terminal alkene gives a primary alcohol whereas hydroboration of a terminal alkyne gives an aldehyde.

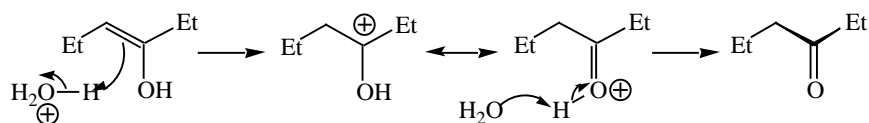


The answer "alkenes and alkynes are different because there is a "y" in alkynes but not in alkenes" is not sufficiently significant.

16. a. Step A (Et = ethyl group = CH₃CH₂):

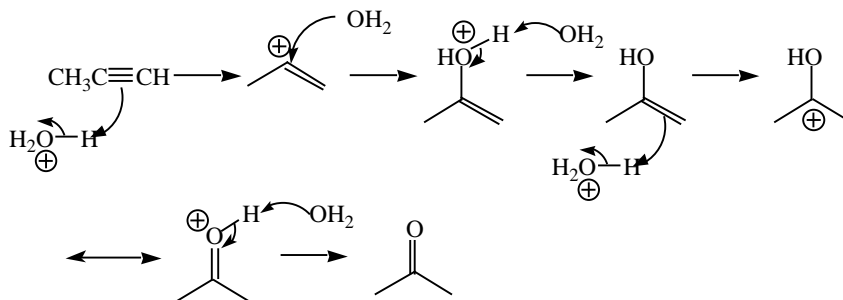


Step B:



b. The rate of these steps is related to the stability of the carbocations products. Step **A** involves a secondary vinylic carbocation (carbocation on an sp carbon of an alkene), whereas step **B** involves a secondary carbocation that has resonance stabilization. The step **B** carbocation is more stable, so step **B** is faster.

17.



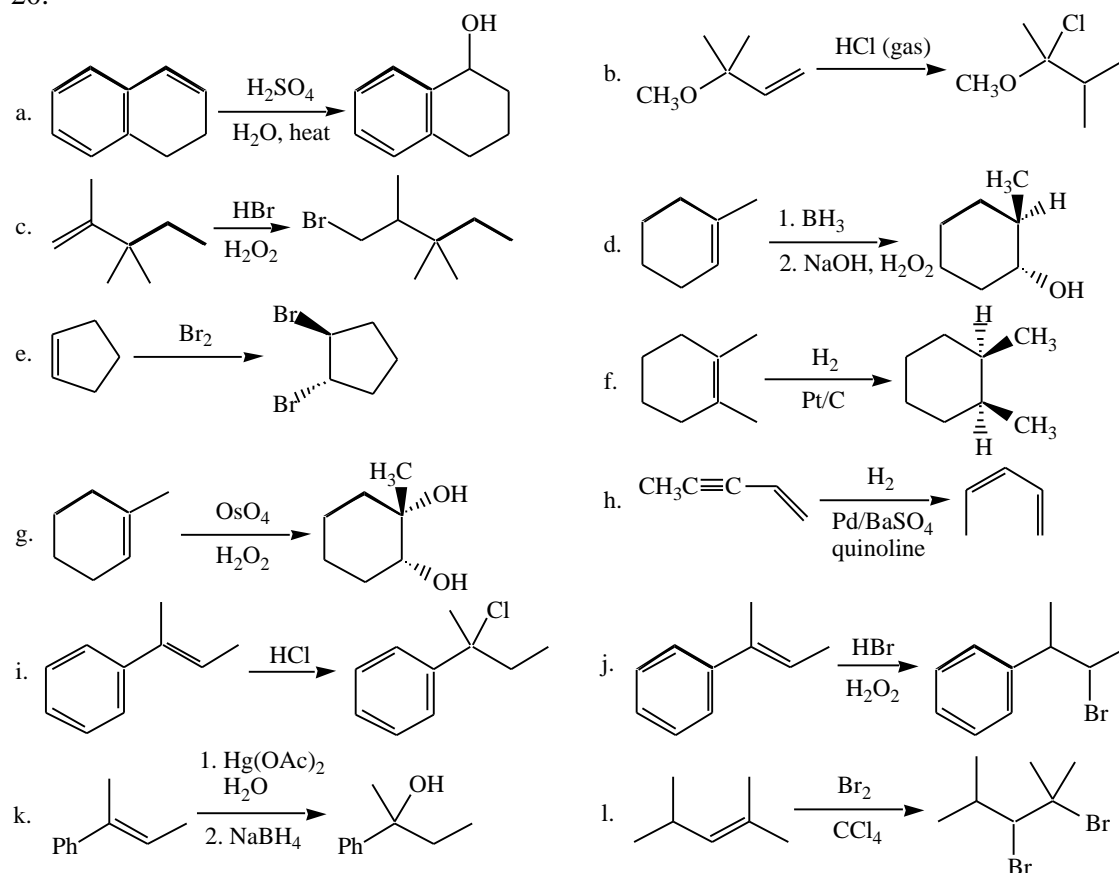
18. BH₃: Borane is electrophilic because boron has only six valence electrons (an open octet). Hg(OAc)₂: Mercuric acetate is an electrophile after it ionizes to form ⁺HgOAc and acetate ion (⁻OAc). The ⁺HgOAc cation is electrophilic because it bears a full positive charge.

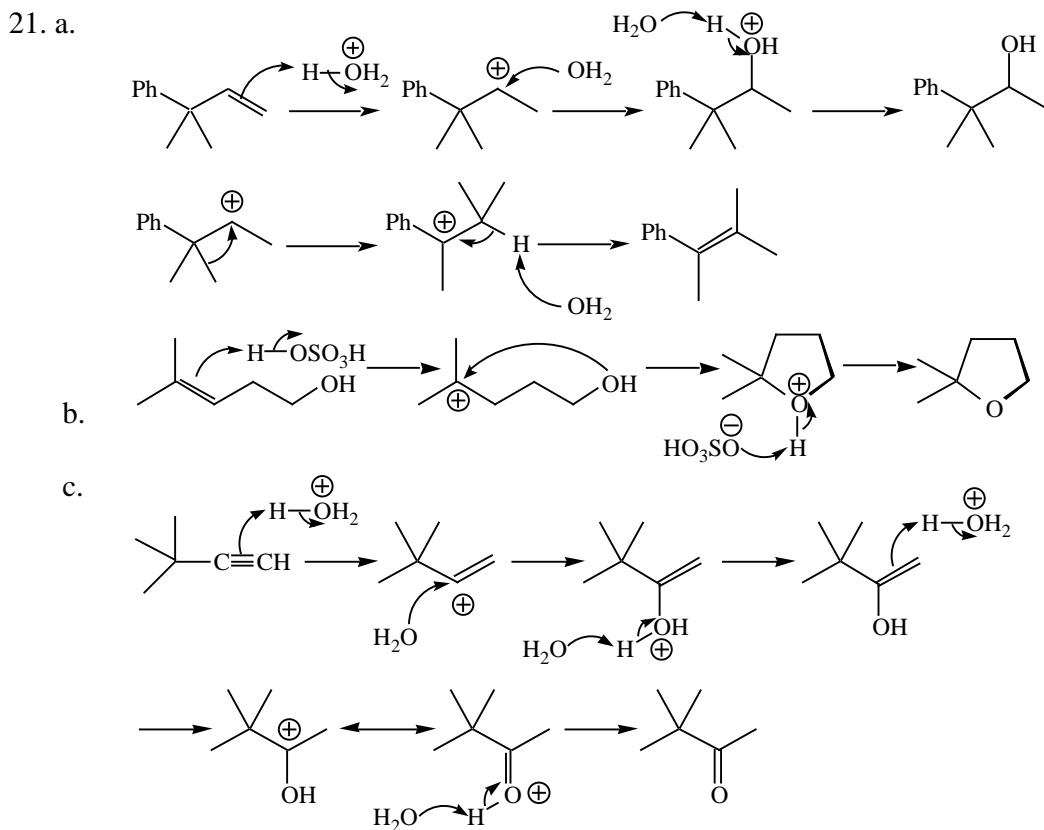
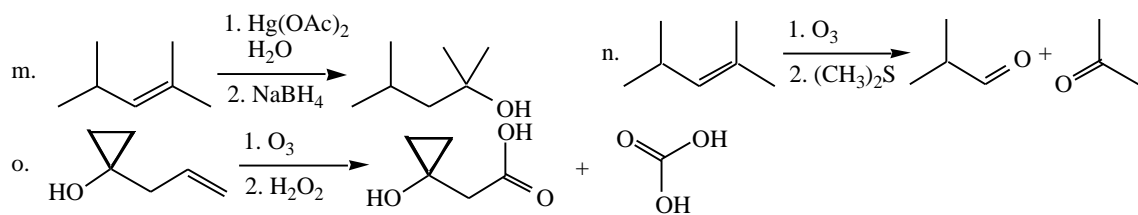
19.

Reactant	Reaction Type	Reaction with Isobutylene
HBr (gas)	electrophilic addition	
H ₃ O ⁺	electrophilic addition	
BH ₃	electrophilic addition	

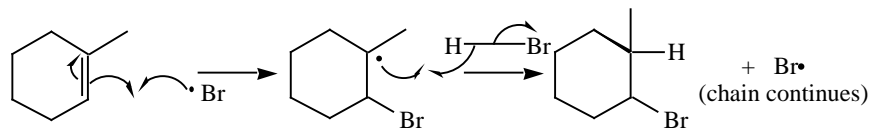
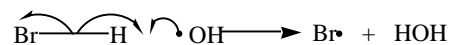
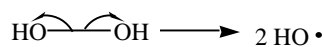
H ₂	other	
O ₃	other	
OsO ₄	other	
HBr/H ₂ O ₂	electrophilic addition	
Br ₂	electrophilic addition	
Hg(OAc) ₂	electrophilic addition	

20.

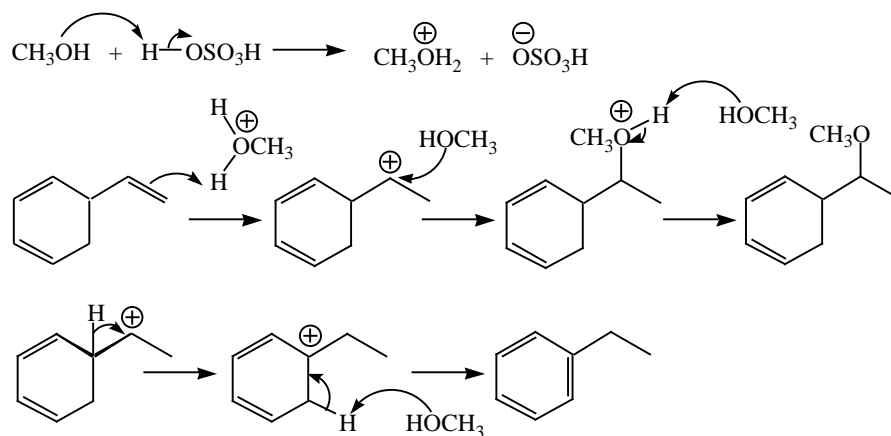




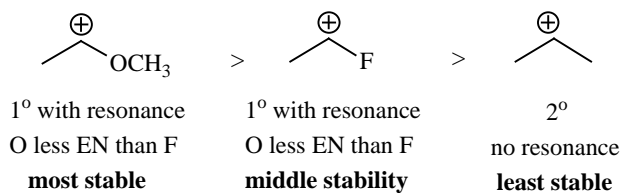
d. The presence of molecular oxygen (O_2) or peroxides (such as H_2O_2) often, but not always, suggest the reaction mechanism involves radicals.



e. Protonation of an alkene forms a carbocation with an open octet, whereas protonation of methanol does not form an open octet. Thus we predict methanol to be a stronger base than the alkene. The mechanism starts with the stronger base reaction with sulfuric acid.

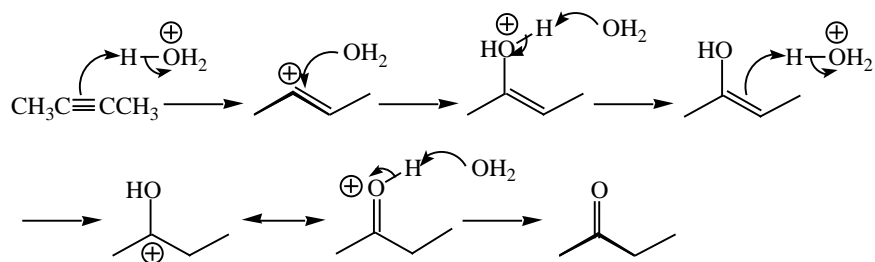


22. The rate-determining step for the electrophilic addition to an alkene is formation of the carbocation. Carbocations that are more stable will be formed more quickly. For this answer, we will assume the electrophile is HBr, but as long as the alkenes are reacted with the same electrophile the structure of the electrophile is irrelevant. The carbocations formed from vinyl fluoride ($\text{H}_2\text{C}=\text{CHF}$) and methyl vinyl ether ($\text{H}_2\text{C}=\text{CHOCH}_3$) both are primary with resonance. (Recall that fluorine has three lone pairs, and that we generally consider resonance to be more important than electronegativity or inductive effects.) Fluorine is more electronegative than oxygen, so fluorine will be less inclined to share electrons through resonance. Thus we predict the cation from vinyl fluoride to be less stable than the cation from methyl vinyl ether. The carbocation formed from electrophilic addition to propene ($\text{H}_2\text{C}=\text{CHCH}_3$) is secondary, and so less stable than either of the carbocations that are primary with resonance. The order of carbocation stability is:

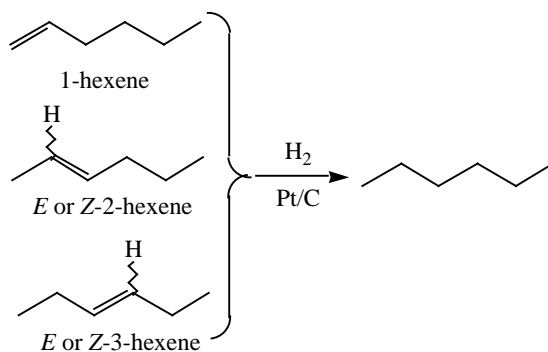


Therefore the order of electrophilic addition rate is $\text{H}_2\text{C}=\text{CHOCH}_3$ (fastest) > $\text{H}_2\text{C}=\text{CHF}$ > $\text{H}_2\text{C}=\text{CHCH}_3$ (slowest).

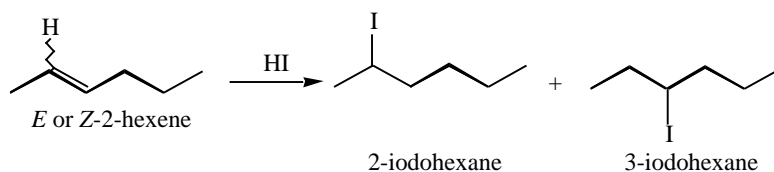
23. The rate-determining step in the alkyne hydration reaction is attack of hydronium ion to form the vinyl carbocation. Carbocation stability determines which reaction is faster. The carbocation formed in the first two reactions are secondary whereas the carbocation from the third reaction is primary and thus has a higher E_{act} . A methyl group is electron-donating (stabilizes a carbocation) whereas a trifluoromethyl group is a much weaker electron donating group due to the inductive effect of the three fluorine atoms. (In fact, the combined inductive effect of the three fluorine atoms overrides the weak inductive donating effect, rendering CF_3 a weak electron-withdrawing group.) Thus, the first reaction is fastest.



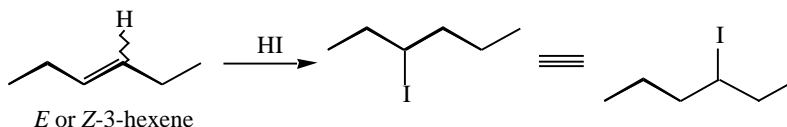
24. There are three alkenes that can undergo catalytic hydrogenation to give n-hexane.



Of these alkenes, 1-hexene has a single stereoisomers (cannot be E and Z), so it is excluded. Reaction of either 2-hexene stereoisomer with HI gives two alkyl iodides, so 2-hexene is excluded. (The wavy C-H bond indicates the stereochemistry at this atom is a mixture, is unknown, or is undetermined.)



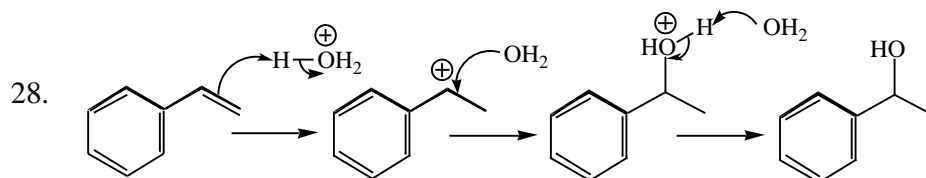
The two alkyl iodides formed from the reaction of either E or Z-3-hexene are identical (3-iodohexane), so 3-hexene is the correct answer.



25. In the presence of peroxides, the electrophile is bromine radical. This adds to the alkene to form the most stable radical intermediate, resulting in the bromine becoming bonded to the least substituted carbon of what was the alkene. When HBr attacks an alkene, the hydrogen end of HBr becomes attached to the least substituted end of the alkene to form the more stable carbocation. Capture of bromide ion by the

carbocation then leads to the product in which the bromide atom is bonded to the carbon that was the more substituted end of the alkene.

26. These reagents have a similar $O=X=O$ structure, where X is an electron-deficient atom (Os^{8+} or O^+). Each concerted cycloaddition reaction is driven by the reduction of X (gains a pair of electrons), as well as an exchange of π for σ bonds. Each reaction has a five-membered ring intermediate, in which the two new C-O bonds are syn. The fate of this intermediate controls the final reaction products.
27. Reaction of an alkene with a carbocation affords a new carbocation product. The cyclization mode that forms the most stable carbocation will be favored. (Compare this with the mechanistic reason for Markovnikov's rule.) Cyclization to form a cyclohexane A ring gives a tertiary carbocation, whereas cyclization to afford a cyclopentane A ring would proceed through a secondary carbocation. Because a tertiary carbocation is easier to form than a secondary carbocation, the cyclohexane cyclization pathway is favored over the cyclopentane cyclization pathway.



The position of the HO group in the final product is determined by which carbocation is formed in the first mechanism step. In any reaction where a carbocation is formed, the more stable carbocation will be favored. Protonation of the CH_2 end of the alkene affords a carbocation that is secondary and has resonance. Protonation of the benzylic carbon (the carbon directly bonded to the benzene ring) affords a carbocation that is primary and has no resonance. Because the former carbocation is more stable, the reaction product is the secondary (not primary) alcohol. This is an example of Markovnikov addition.