Objective 10: Apply reactivity principles to Elimination reactions: identify structural features (alpha C, H on beta C, LG), use curved arrows to predict product, compare E1 vs. E2 mechanisms.

Quiz Practice problems

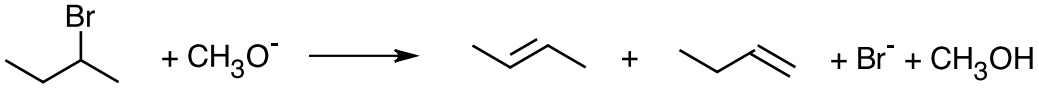
Key ideas:

Elimination reactions are used to make carbon-carbon pi bonds, e.g., alkenes.
In an elimination reaction, a H bonded to a beta carbon, leaving group, and nucleophile are needed.
The beta carbon is the carbon bonded to an alpha carbon.
The alpha carbon is the carbon bonded to a leaving group.
A leaving group is a base – see pK_a table.
Leaving groups can be good or poor.
A good leaving group is a weak base. A good leaving group is needed for a substitution reaction to occur.
A poor leaving group can be made into a good leaving group.
A nucleophile reacts at the alpha carbon and substitutes for the leaving group.

Skills:

Identify alpha carbon in a compound.
Identify H bonded to beta carbon in a compound.
Identify alpha carbon as 1^o, 2^o, 3^o.
Identify leaving group in a compound.
Identify leaving group as good or poor.
Describe how to make a poor leaving group into a good leaving group.
Identify a nucleophile as strong or weak.
Given reactants, use curved arrows to show how nucleophile reacts at H bonded to beta carbon to form elimination products.
Identify the more stable product (major product).
Describe a elimination reaction using a E1 mechanism.
Describe a elimination reaction using a E2 mechanism.

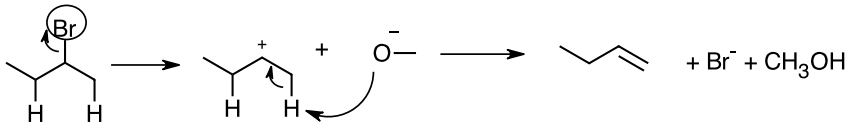
1. 2-bromobutane reacts with the methoxide ion in an elimination reaction.

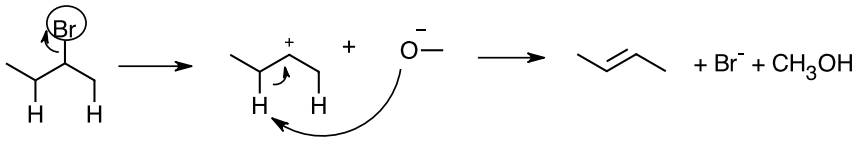


a. Draw in the H bonded to the beta carbon and circle the leaving group in the reactants. Is the leaving group good or poor?
b. CH_3O^- is a nucleophile. Is this nucleophile strong or weak?
c. This reaction can occur by a E1 or E2 mechanism.
(i) Use curved arrows to show how reactants form products in a E1 mechanism.
(ii) Use curved arrows to show how reactants form products in a E2 mechanism.
d. Which alkene is the major product?

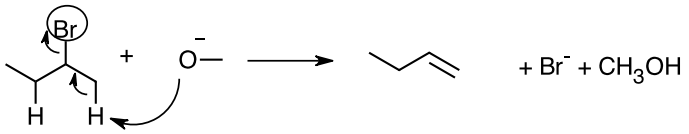
Answers:

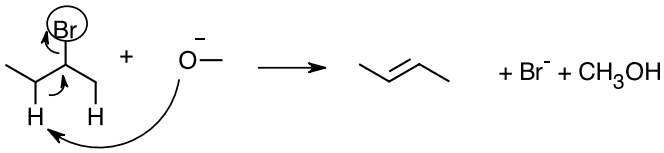
a. Br is a good leaving group because it is a weak base – see pK_a table.
b. CH_3O^- is a strong nucleophile because it is a strong base – see pK_a table.
c The reactant is a 2^o alkyl bromide so the reaction can occur by a E1 or E2 mechanism.
(i). E1 mechanism





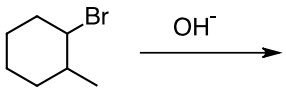
(ii). E2 mechanism



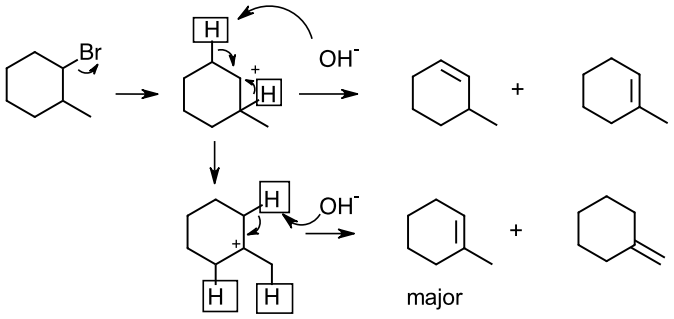


d. The more substituted alkene is more stable.
The more stable alkene is the major product.
Major product is 2-butene (with C=C bond between C2 and C3).

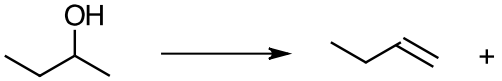
2. A carbocation intermediate forms in a E1 mechanism. A carbocation can rearrange to a more stable carbocation by a hydride ($H:^-$) shift or alkyl ($R:^-$) shift.
This reaction produces more than two organic elimination products. Draw the structures of each organic elimination product. Use curved arrows to show how each product forms.



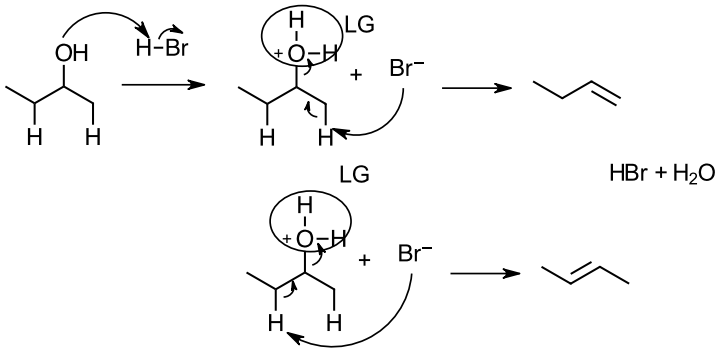
Answers: The H on each beta carbon is boxed.
The 3^o carbocation is more stable than the 2^o carbocation.
The major product is shown. This compound is a tri-substituted alkene.



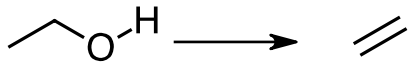
3. Explain why HBr is the other reactant and not Br^-. Use curved arrows to show how reactants form the product shown and a 2^{nd} alkene. Identify the H bonded to the beta carbon, leaving group, and nucleophile. Which alkene is the major product? (Hint: see Zaitsev's rule)



Answers:
-OH is a poor leaving group because it is a strong base. So ROH will not react with Br^- in an elimination reaction.
HBr reacts with ROH to form ROH_2^+; H_2O is a better leaving group because it is a weak base.
H's on beta C are shown.
2-butene is the major product. It is a disubstituted alkene and more stable than 1-butene, which is a monosubstituted alkene.



4. a. Would you use C_2H_5OH or $C_2H_5O^-$ to make this reaction occur? Use curved arrows to show how reactants form products. Identify the H bonded to the beta carbon, leaving group, and nucleophile.

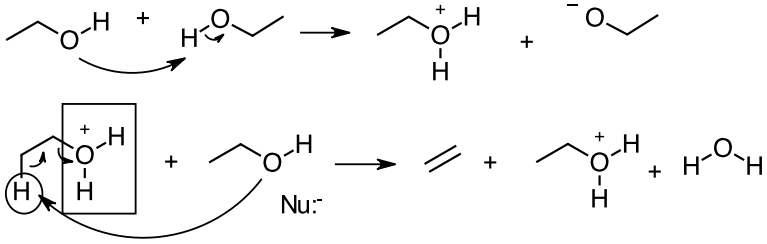


b. Draw the structure of another reactant (with a different functional group) to make the product in part a.

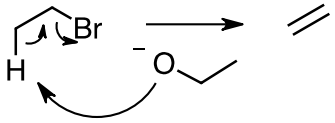
Answers:

a. Use C_2H_5OH. See Objective 9 Question 4.

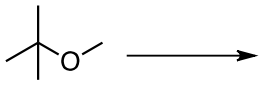
In 2nd step, H bonded to beta carbon is circled, leaving group is boxed, and C_2H_5OH is the nucleophile.



b. Use C_2H_5Br.



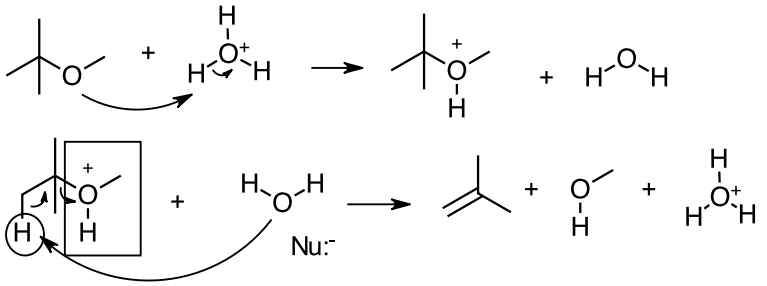
5. An acid catalyst, e.g., H_3O^+, is needed for this reaction to occur. Use curved arrows to show how reactants form the elimination product. Identify the H bonded to the beta carbon, leaving group, and nucleophile.



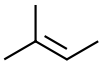
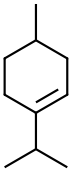
Answers:

H_3O^+ is needed to make the ether group (RO^-) into a better leaving group (ROH).

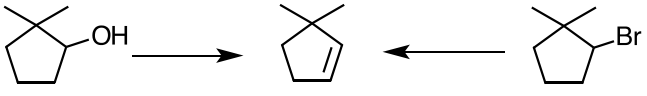
In 2nd step, H bonded to beta carbon is circled, leaving group is boxed, and H_2O is the nucleophile.



6. Elimination reactions are used to make carbon-carbon pi bonds, e.g., alkenes. Identify the reactants to make the following alkenes:

a.  b.  c. 

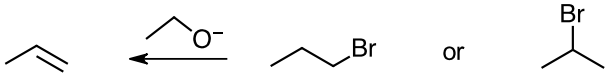
d. You have available 2,2-dimethylcyclopentanol (A) and 2-bromo-1,1-dimethylcyclopentane (B) and wish to prepare 3,3-dimethylcyclopentene (C). Which would you choose as the more suitable reactant, A or B, and with what would you treat it?

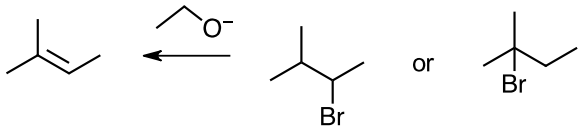


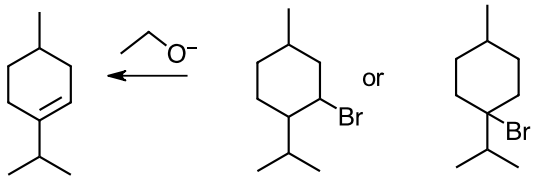
A C B

Answers:

Remember, a H bonded to a beta carbon, leaving group, and nucleophile are needed in an elimination reaction to form a C=C bond. The pi bond forms between the alpha and beta carbons.

a. 

b. 

c. 

d. React A with H_2SO_4 or H_3O^+ to form C.

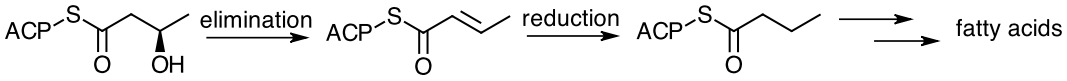
React B with $C_2H_5O^-$ to form C.

B works better because the stronger $C_2H_5O^-$ nucleophile reacts faster than the weaker H_2O nucleophile.

7. There are many examples of elimination reactions in biology.

a. Fatty acid biosynthesis

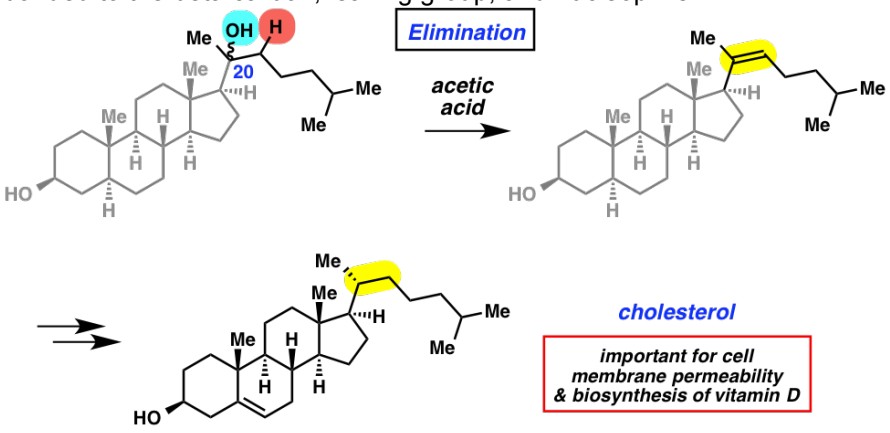
β-hydroxy butyryl-ACP –– elimination --> crotonyl-ACP – reduction --> -->--> fatty acids



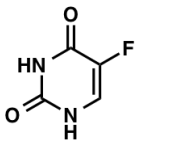
B-hydroxy butyryl-ACP crotonyl-ACP

Identify the H bonded to the beta carbon and leaving group.

b. From LearnBacon.com: Woodward's 1952 synthesis of cholesterol involved an elimination reaction. Identify the H bonded to the beta carbon, leaving group, and nucleophile.



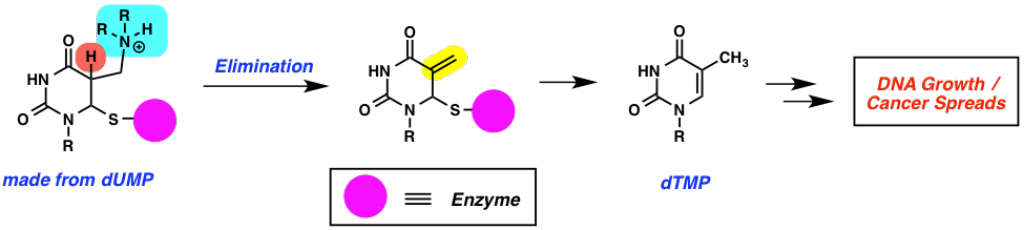
c. From LearnBacon.com: Fluorouracil – anti-cancer drug. The mechanism of action is an elimination reaction. Identify the H bonded to the beta carbon and leaving group.



Fluorouracil

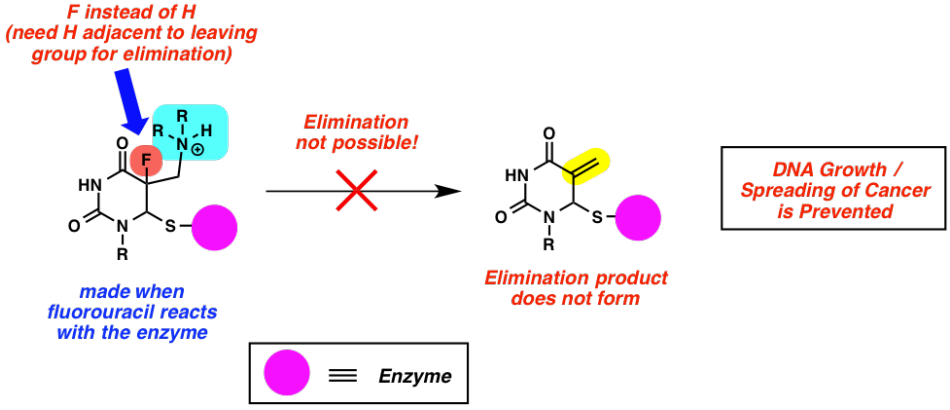
anti-cancer drug

How a cancer cell divides:



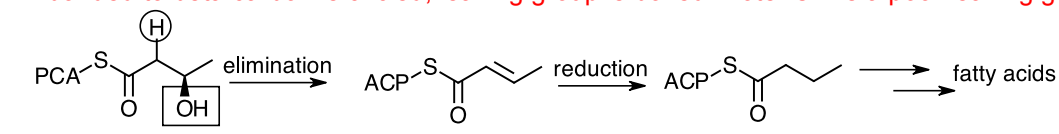
Thymidylate synthase converts deoxyuridinemonophosphate (dUMP) to deoxythymidinemonophosphate (dTMP). One step is an elimination reaction.

Fluorouracil is an anti-cancer drug (breast, skin, stomach, pancreatic, colon cancers). How does fluorouracil work? Replace H by F and no elimination reaction.



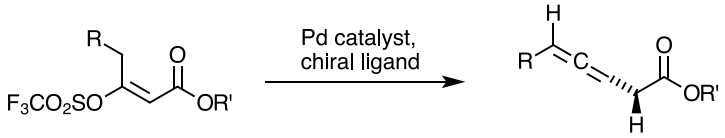
Answers:

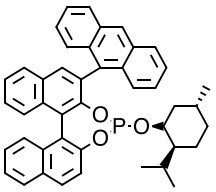
a. H bonded to beta carbon is circled, leaving group is boxed. Note: OH is a poor leaving group.



b. Acetic acid reacts with OH (circled in blue) to form ROH_2^+, which is a better leaving group.
$CH_3COOH + ROH \rightarrow ROH_2^+ + CH_3COO^-$
The H circled in red is the H bonded to the beta carbon. Acetate ion (the conjugate base of acetic acid) is the nucleophile.
CH_3COO^- reacts at H bonded to beta C ---> alkene + CH_3COOH + H_2O (leaving group)
c. The H circled in red is the H bonded to the beta carbon. The NR_2H group circled in blue is the leaving group.

8. 4/1/13, CEN, p. 38 “Elimination Reaction Cooks Up Chiral Allenes” (http://cen.acs.org/articles/91/i13/Elimination-Reaction-Cooks-Chiral-Allenes.html)





This is an elimination reaction. The leaving group in the reactant is $–OSO_2CF_3$.

a. Something is wrong with the structure of the product. What is wrong?

b. Draw the correct structure of the product.

Answers:

a. The product has one more carbon (5 carbon chain excluding R) than the reactant (4 carbon chain excluding R).

b. Note: in the product, the C with two pi bonds is linear with sp hydridization.