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

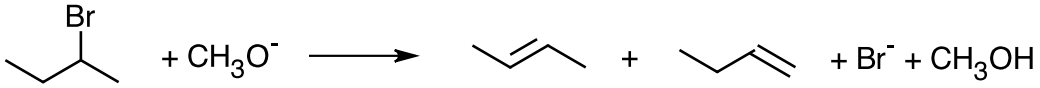
Key ideas:

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:

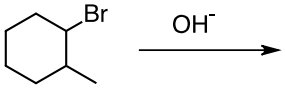
Identify alpha carbon in a compound.
Identify H bonded to beta carbon in a compound.
Identify alpha carbon as 1^o, 2^o, 3^o.
Identify leaving group in a compound.
Identify leaving group as good or poor.
Describe how to make a poor leaving group into a good leaving group.
Identify a nucleophile as strong 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.

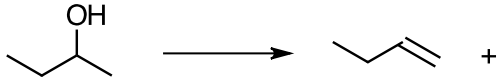


a. Draw in the H bonded to the beta carbon and circle the leaving group in the reactants. Is the leaving group good or poor?
b. CH_3O^- is a nucleophile. Is this nucleophile strong or weak?
c. This reaction can occur by a E1 or E2 mechanism.
(i) Use curved arrows to show how reactants form products in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

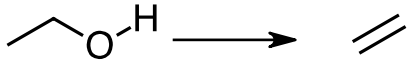
2. A carbocation intermediate forms in a E1 mechanism. A carbocation can rearrange to a more stable carbocation by a hydride ($H:^-$) shift or alkyl ($R:^-$) shift.
This reaction produces more than two organic elimination products. Draw the structures of each organic elimination product. Use curved arrows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



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)

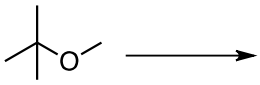


4. a. Would you use C_2H_5OH or $C_2H_5O^-$ to make this reaction occur? Use curved arrows to show how reactants form products. Identify the H bonded to the beta carbon, leaving group, and nucleophile.



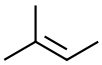
b. Draw the structure of another reactant (with a different functional group) to make the product in part a.

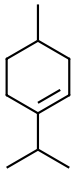
5. An acid catalyst, e.g., H_3O^+, is needed for this reaction to occur. Use curved arrows to show how reactants form the elimination product. Identify the H bonded to the beta carbon, leaving group, and nucleophile.



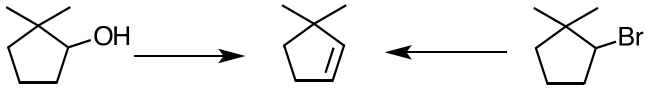
6. Elimination reactions are used to make carbon-carbon pi bonds, e.g., alkenes. Identify the reactants to make the following alkenes:

a. 

b. 

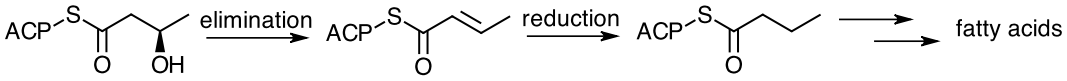
c. 

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

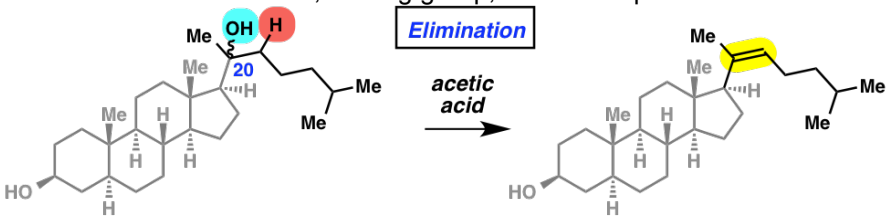
7. There are many examples of elimination reactions in biology.
a. Fatty acid biosynthesis
β-hydroxy butyryl-ACP — elimination --> crotonyl-ACP – reduction --> -->--> fatty acids

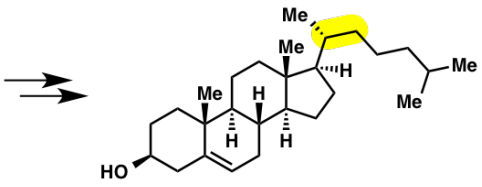


B-hydroxy butyryl-ACP crotonyl-ACP

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.

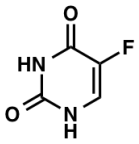




cholesterol

important for cell membrane permeability & biosynthesis of vitamin D

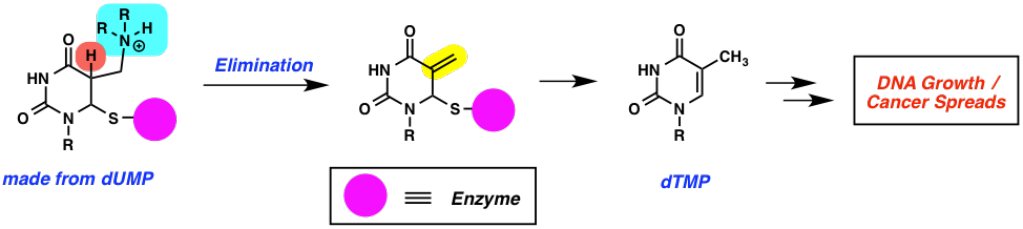
c. From LearnBacon.com: Fluorouracil – anti-cancer drug. The mechanism of action is an elimination reaction. Identify the H bonded to the beta carbon and leaving group.



Fluorouracil

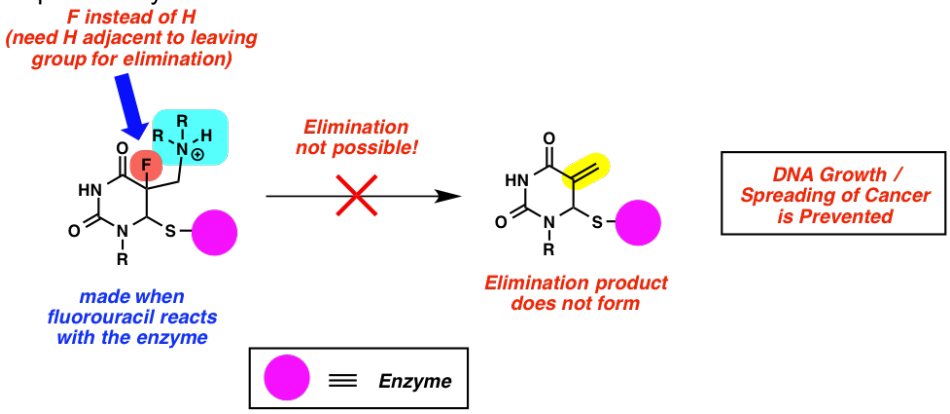
anti-cancer drug

How a cancer cell divides:

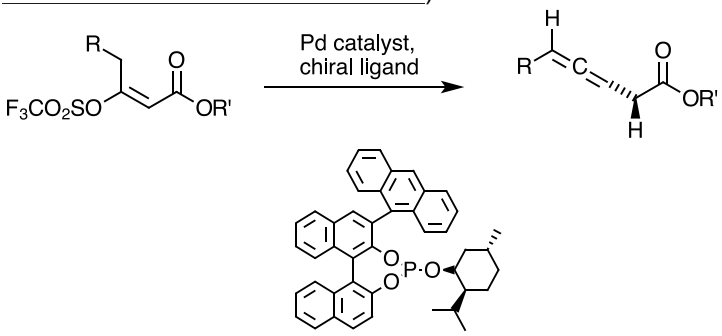


Thymidylate synthase converts deoxyuridinemonophosphate (dUMP) to deoxythymidinemonophosphate (dTMP). One step is an elimination reaction.

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



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.