Topics: Unsaturation Number (revisited), Intro to Synthesis

OCSP 2020
Lecture #9 BP, AF
July 10th, 2020

- Unsaturation Number (also known as Degree of Unsaturation): Indicates the total number of pi bonds and rings within a molecule which makes it easier to figure out the molecular structure just from the molecular formula.

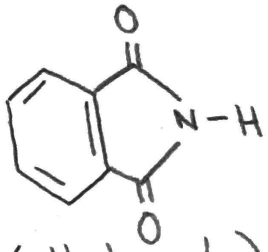
Degree of Unsaturation (DofU) = (number of pi bonds) + (number of rings)

→ Example:


(benzene)

H−C≡C−H
(acetylene)


(butane)



(pthalamide)

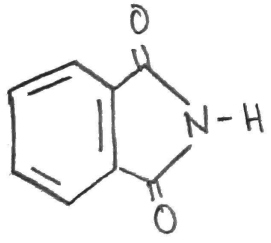
DofU: 4 (1 ring, 3 π bonds) | 2 (0 rings, 2 π bonds) | 0 (0 rings, 0 π bonds) | 7 (2 rings, 5 π bonds)

- So, how can we calculate the DofU from just the molecular formula?

→ Equation 1:

$$DofU = \frac{2C + 2 + N - X - H}{2}$$

(2 times # of carbons; # of nitrogens; # of halides (Cl, F, Br, etc.); # of hydrogens)

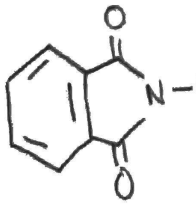



$DofU = \frac{2(8)+2+1-0-5}{2} = \frac{19-5}{2} = 7$

$(C_8H_5NO_2)$

→ Equation 2:

$$DofU = 1 + \frac{1}{2}\left(\sum (\#\text{ of atom})(\#\text{ of bonds atom forms} - 2)\right)$$




$$DofU = 1 + \frac{1}{2}\left(\sum (8\cdot(4-2)) + (5\cdot(1-2)) + (1\cdot(3-2)) + (2\cdot(2-2))\right)$$

(carbon normally forms 4 bonds; hydrogen forms 1 bond; nitrogen forms 3 bonds; oxygen forms 2 bonds)

$$= 1 + \frac{1}{2}[16 - 5 + 1 + 0] = 1 + \frac{1}{2}[12] = 7$$

$(C_8H_5NO_2)$

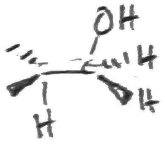
- Key Point: You may be given either equation so try to be comfortable with both (but you can have a preference). Whenever you're given a molecular formula (with no molecular structure), calculate D of U.

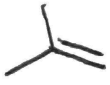
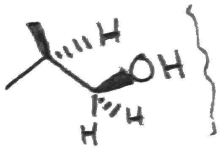
- Introduction to Synthesis: A synthesis is a series of two or more reactions designed to obtain a specific final product

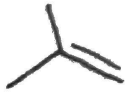
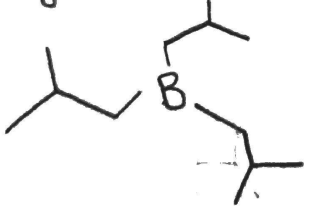
  - The secret to synthesis... (or retrosynthesis)

    1. Look for patterns
       - What functional group is present on the reactant?
       - What functional group is present on the product?
       - Which reactions do I know to convert one to the other?
       - Are there any reactants that produce intermediates to the above product?
       - Pay attention to regio & stereochemistry!
    2. When you are stuck, remember there is usually more than one way to get to the product.

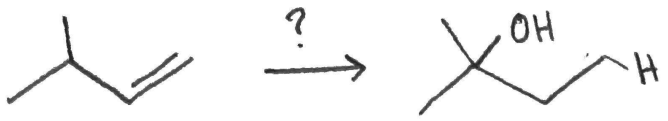
Ex. 1



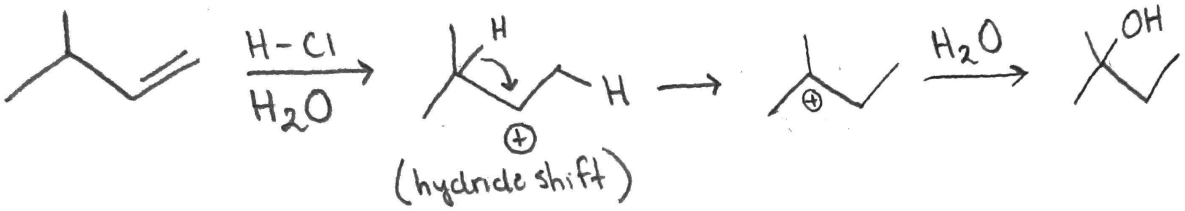
- Let's start with  , how do we get to 
  - We have a reactive pi bond in the reactant
  - We have an alcohol in the product
  - What reactions do we know can add alcohols? (Acid hydration, $BH_3$-THF, $HgOAc_2$)
  - Regiochemistry: note anti-markovnikov add'n
  - Stereochemistry: none given

3  $\xrightarrow{BH_3, THF}$  $\xrightarrow[H_2O]{NaOH, H_2O_2}$ 3 

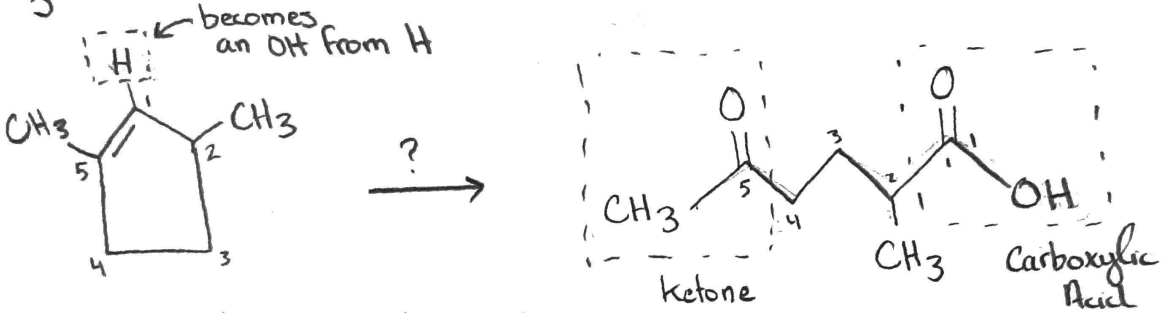
Ex. 2



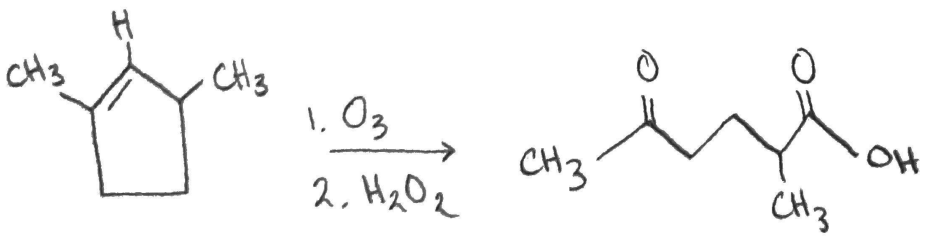

- Reactant has reactive pi bonds
- Product has an alcohol
- How can I add an alcohol? ( $Hg(OAc)_2$, $BH_3$-THF, Acid Hydration )
- No specific stereochemistry and no specific markovnikov or anti-mark.



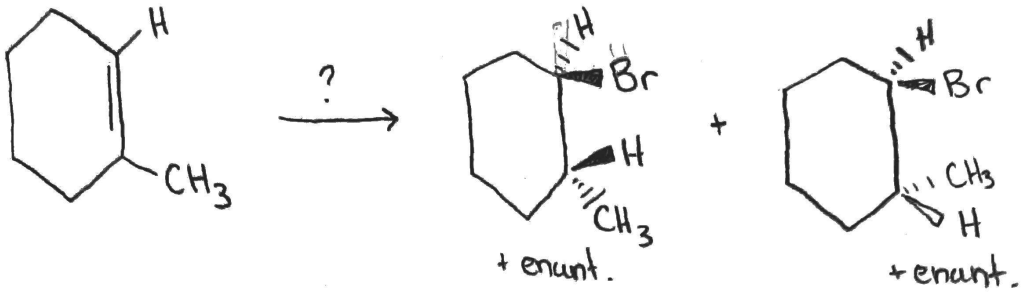

Ex. 3



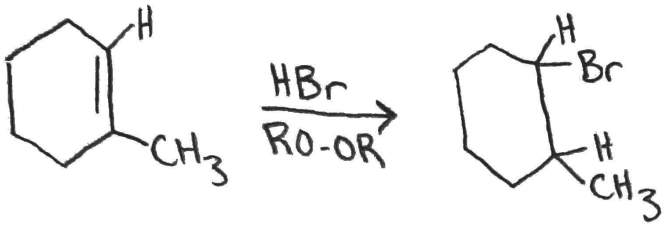

- Reactant has reactive pi bond
- Product has COOH & Ketones
- What mechanisms / reactions can add those functional groups
- No specific stereochemistry or regiochemistry



Ex. 4




- We have added Br to products
- No specific stereochemistry (not stereoselective)
- Note anti-markovnikov regiochemistry




Ex. 5