What mechanisms should you know?
1) Acid catalyzed dehydration / hydration Ch 8
2) H-X addition Ch 8
3) Peroxide ring opening w/ acid Ch 8
4) Keto-enol tautomerism Ch 9
5) Grignard reactions Ch 10

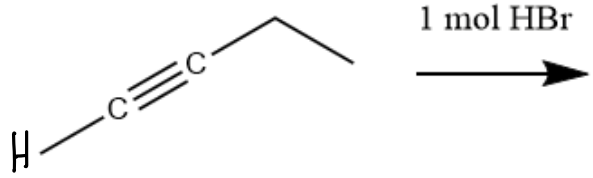
CHEM 223 (2024) SI Session #19

Learning Objectives: By the end of this session, students should be able to:

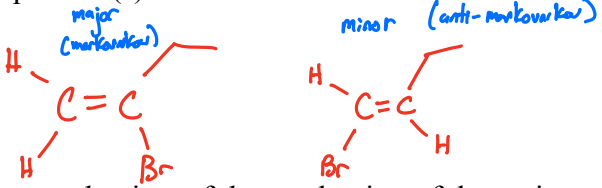
- Predict products and draw mechanisms for alkyne reactions
- Synthesize alcohol products

Section 1: HX addition

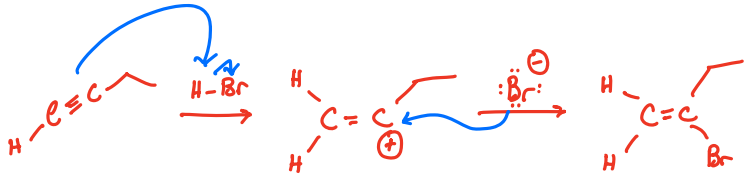
1. Use the following reaction to answer the questions below.



a. Provide product(s) for the reaction.



b. Draw the mechanism of the production of the major product.

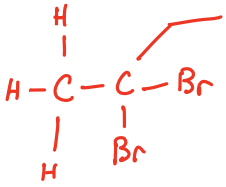


more stable carbocation; more substituted.

c. What do we need to add if we want the minor product in (a) to predominate?

Peroxides (ROOR)

d. If 2 moles of HX are used instead, what's the product?



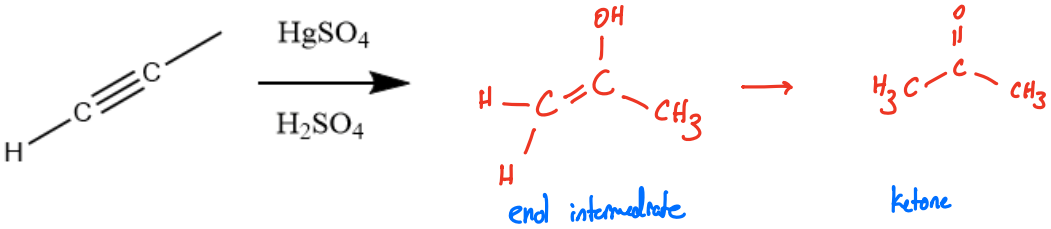
Both bromines to more subs. side.

Section 2: Alkyne hydration, Keto-enol Tautomerism and Oxidation

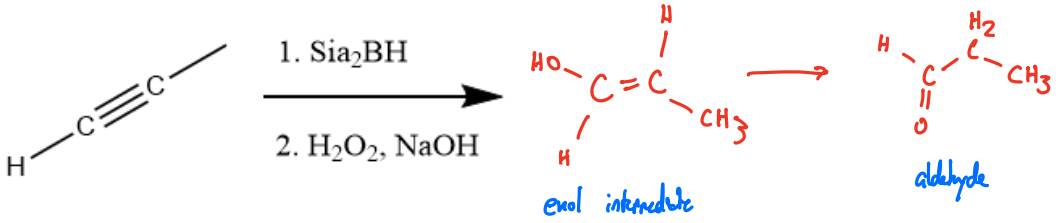
2. For each reaction, draw the unstable intermediate and the product of the reaction.

5:23

a.

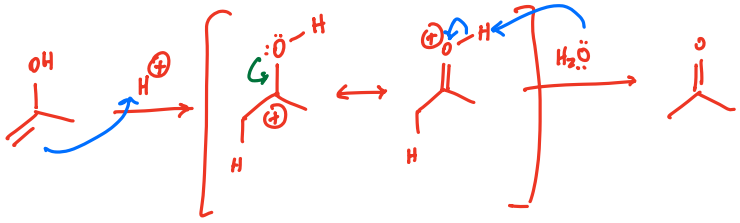


b.



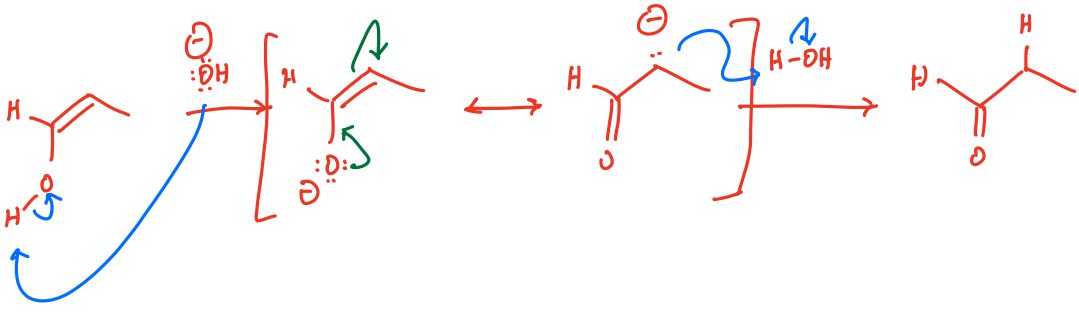
3. Draw the mechanism of the conversion between the intermediate in (a) to the product.

2a is acid catalyzed keto-enol tautomerism



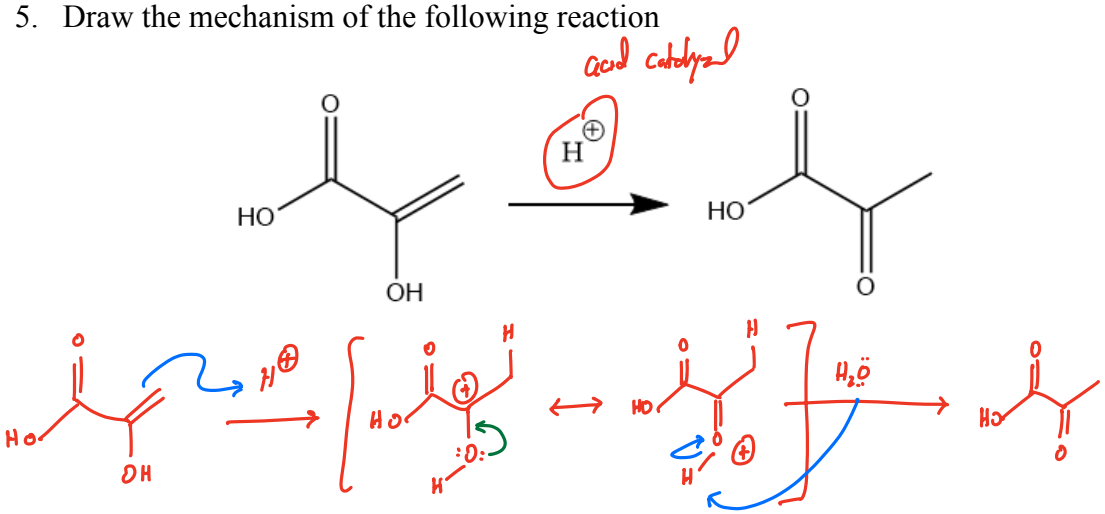
4. Draw the mechanism of the conversion between the intermediate in (b) to the product.

2b is base-catalyzed keto-enol tautomerism



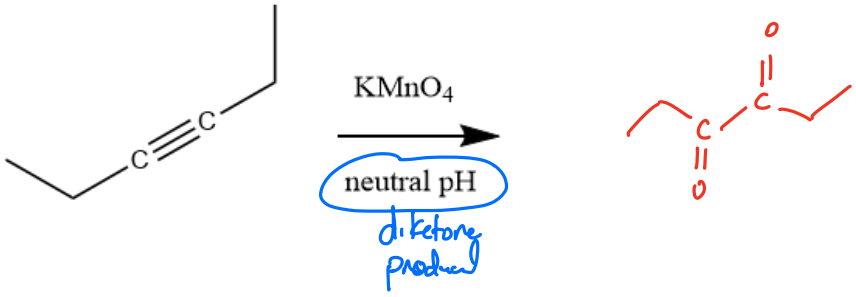
3 & 4 will likely be on the exam.

5. Draw the mechanism of the following reaction

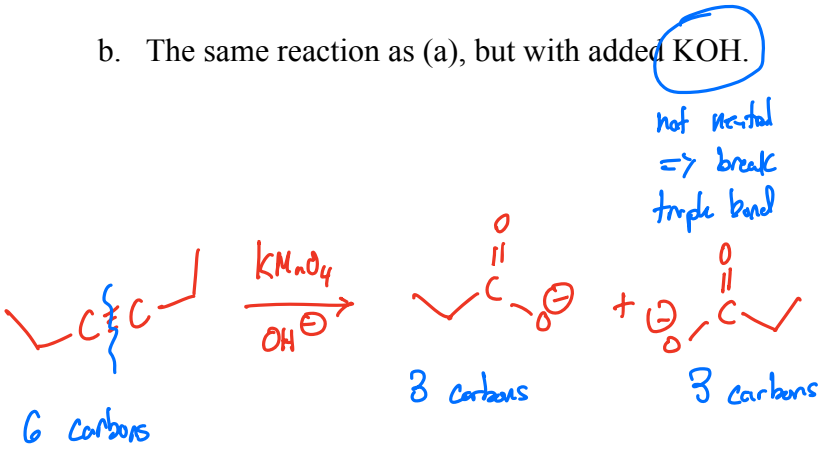


6. Provide products for each of the following reactions

a.

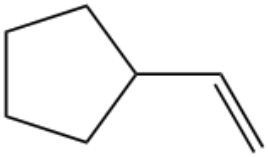


b. The same reaction as (a), but with added KOH.

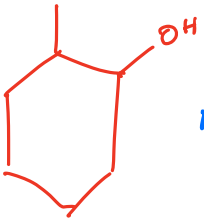


Section 3: Review of alcohol formation methods (start of Ch10)

7. Using the following alkene, draw the major product of the reactions that result in each of the conditions.

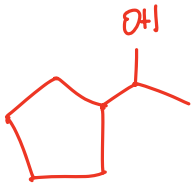


a. Sulfuric acid



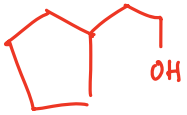
ring expansion occurs

b. 1) $Hg(OAc)_2$, H_2O. 2) $NaBH_4$



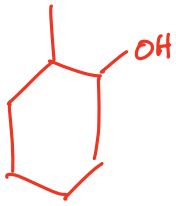
markovnikov OH addition

c. 1) BH_3 THF. 2) H_2O_2, NaOH



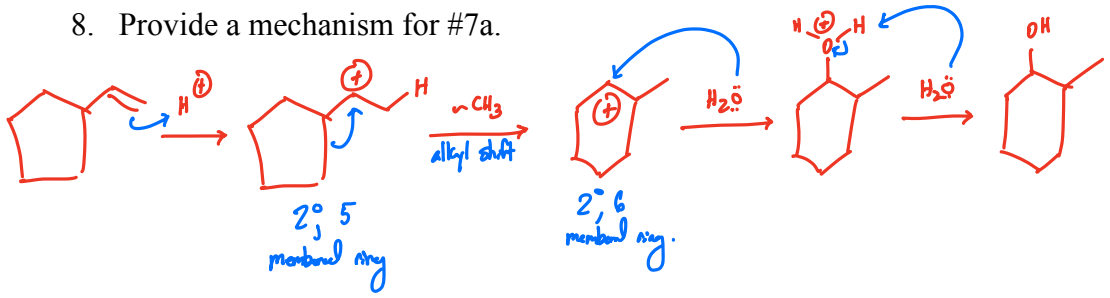
anti-markovnikov OH addition

d. 1) HBr. 2) KOH

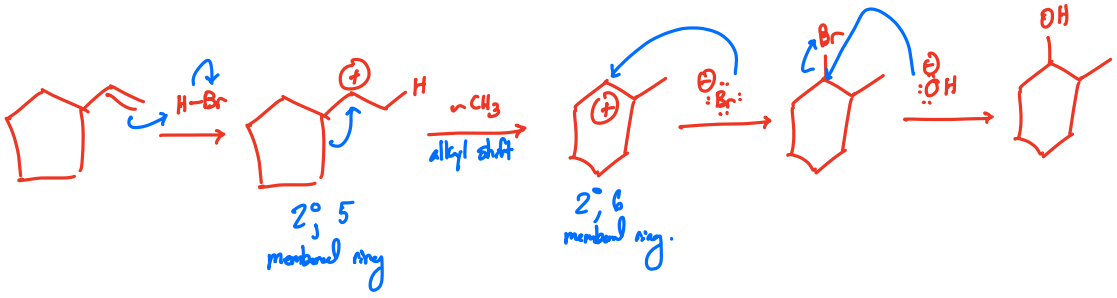


ring expansion will occur.

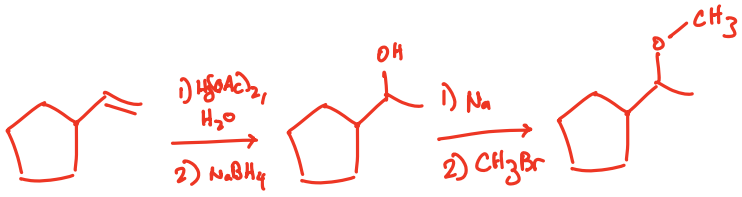
8. Provide a mechanism for #7a.



9. Provide a mechanism for #7d.



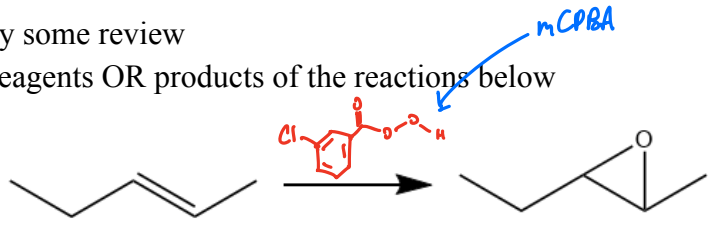
10. Starting from the alkene in #7, synthesize the following compound.



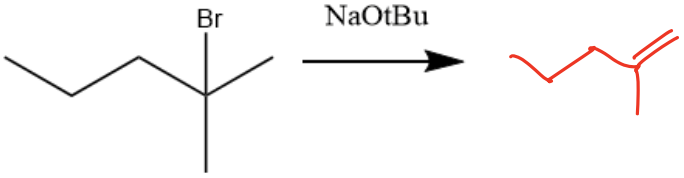
Section 4: Finally some review

11. Provide reagents OR products of the reactions below

a.

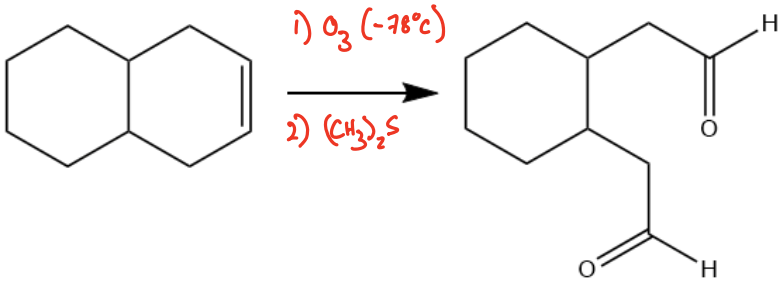


b.



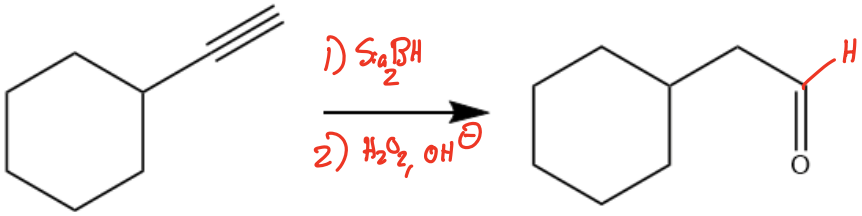
Hoffman product b/c bulky base.

c.



Cleave double bond to produce aldehydes
⇓
ozonolysis

d.

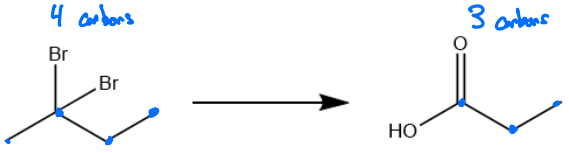


(H hidden)
aldehyde from alkyne => Sia_2BH

e.

12. Provide a synthesis for each of the following compounds (this one is long)

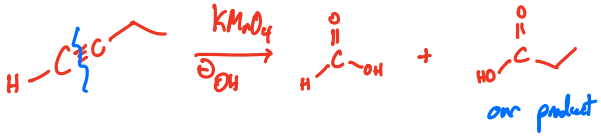
a.



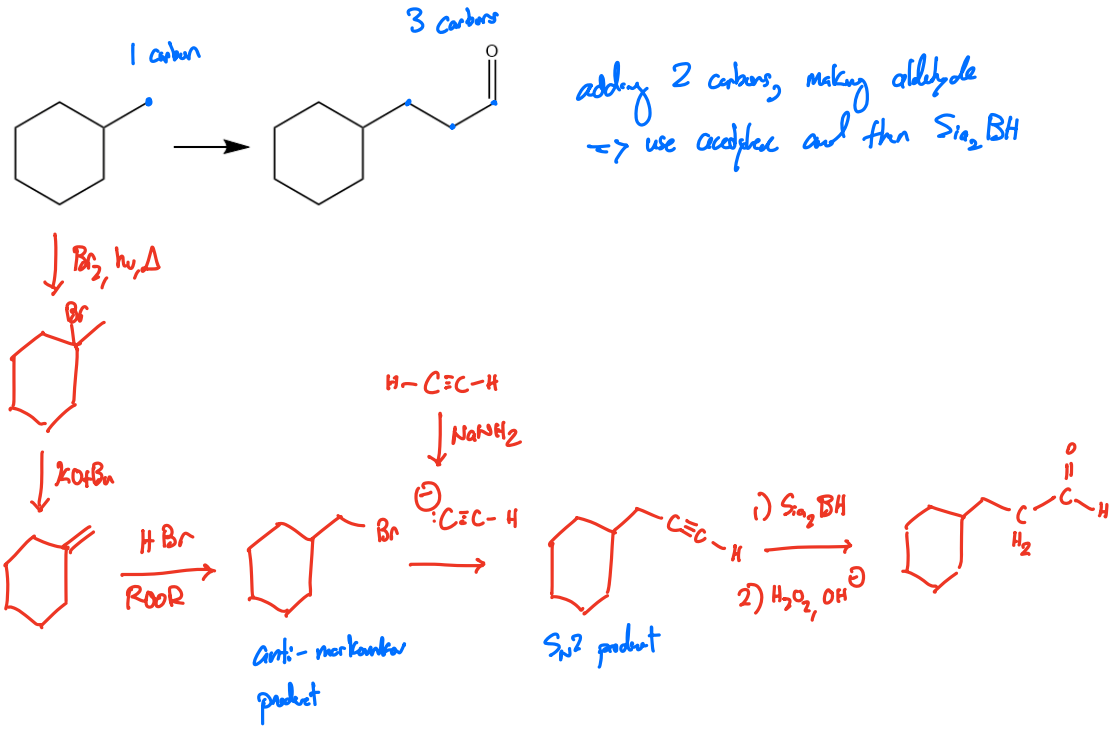
(another product is formed, but we care about this one)

we lose a carbon and make a COOH
=> $KMnO_4$ is used.

$NaNH_2$ favors terminal alkyne
150 °C



b.


1 carbon
3 carbons
O
adding 2 carbons, making aldehyde
=> use acetylene and then Sia_2BH
Br_2, hν, Δ
Br
KOtBu
H Br
ROOR
anti-markovnikov product
H–C≡C–H
$NaNH_2$
⊖ :C≡C–H
S_N2 product
1) Sia_2BH
2) H_2O_2, $OH^⊖$
O
C
H
H_2