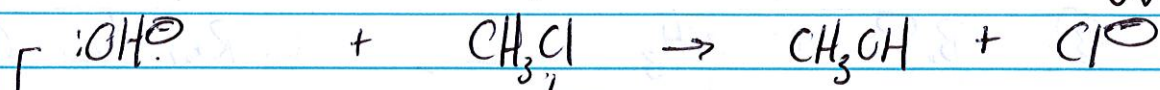


# Chemistry II-AP Mechanistic Chemistry

## I. Substitution Reactions

- Overall reaction:

Nucleophile + electrophile  $\rightarrow$  product + leaving group



$\rightarrow$  nucleophiles have the minimum characteristic of having a lone pair. ~~Can be~~ 1°

Can be 1°, 2°, or 3°  
(show ex:)

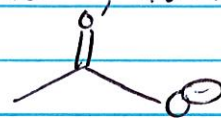
- Substitution reactions diversify the type of chemistry you are allowed to do. It's unlike the boring free radical halogenation.  
For example:

How do I make bromoethane  $\text{CH}_3\text{CH}_2\text{Br}$  if there is no bromine (liquid) in the house?  
All other reagents are available.



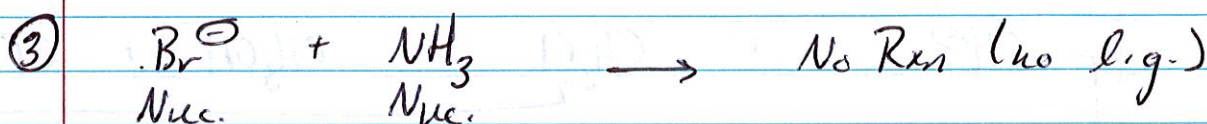
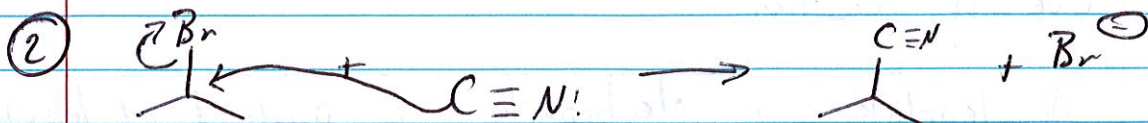
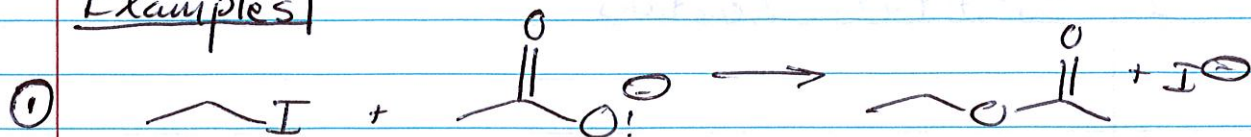
Table 1: Nucleophiles

Degree	Examples
Strong	$\text{I}^-$ , $\text{HS}^-$ , $\text{RS}^-$ (large size)
Good	$\text{Br}^-$ , $\text{OH}^-$ , $\text{RO}^-$ , $:\text{CN}^-$ , $:\text{N}=\text{N}=\text{N}^-$ (azide)
Fair	$\text{NH}_3$ , $\text{Cl}^-$ , $\text{F}^-$
Weak	$\text{H}_2\text{O}$ , $\text{ROH}$



- Be it strong or weak, all will do the job.

### Examples



Halogen attached to C, not an electrophile.

- These are all examples of  $\text{S}_{\text{N}}2$  mechanisms. Substitution, nucleophilic, bimolecular.

$\rightarrow$   $\text{S}_{\text{N}}2$  mechanisms occur with methyl,  $1^\circ$  and  $2^\circ$  electrophiles.

- measuring the rates of reactions has determined that the rate is dependent on the [nucleophile] and the [alkyl halide].

$$\text{Rate} = k[\text{electrophile}][\text{nucleophile}]$$

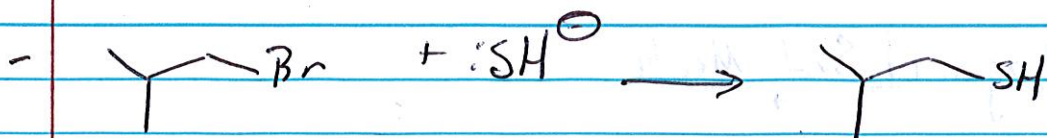
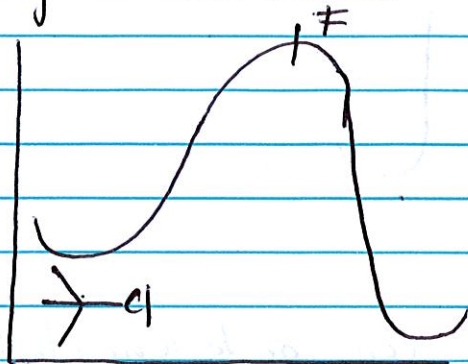


Diagram / S<sub>N</sub>2 Mech



① Rate =  $k_c [\text{Nuc}] [\text{Elec}]$

Collision-state theory

methyl, 1°, 2° electrophiles

- Naturally, what happens to 3° electrophiles?  
What type of mechanistic chemistry do they follow?



3° elect.

The products are as you expected. The mechanism is different.

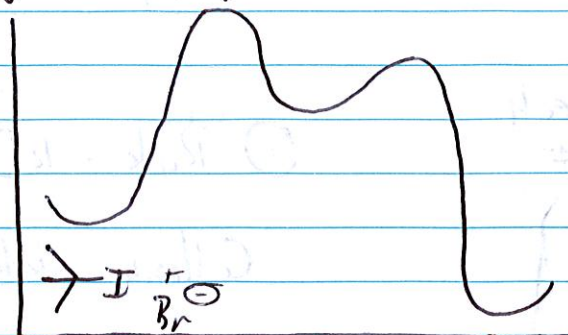
Mech



Why?

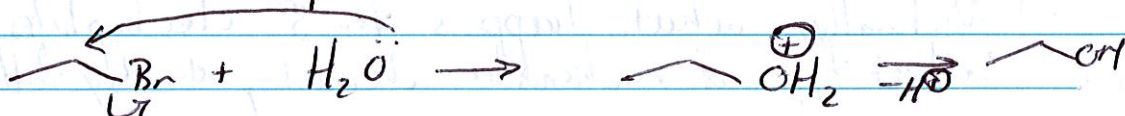
In order for a reaction to occur a transition state must happen (temporarily). ~~with 3° electrophiles~~ the carbon would have 5 "bonds". We call this interaction steric hindrance. There is not enough room.

Diagram / S<sub>N</sub>1 Mech

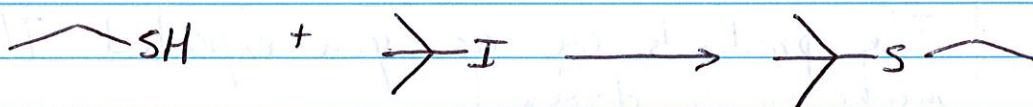


Rate = k [electrophile]

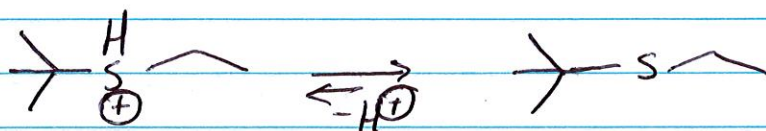
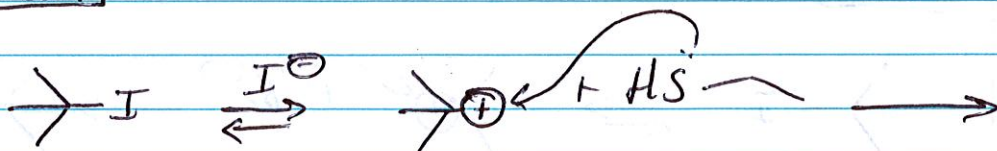
- Side Note: If you can, go to a neutral product.

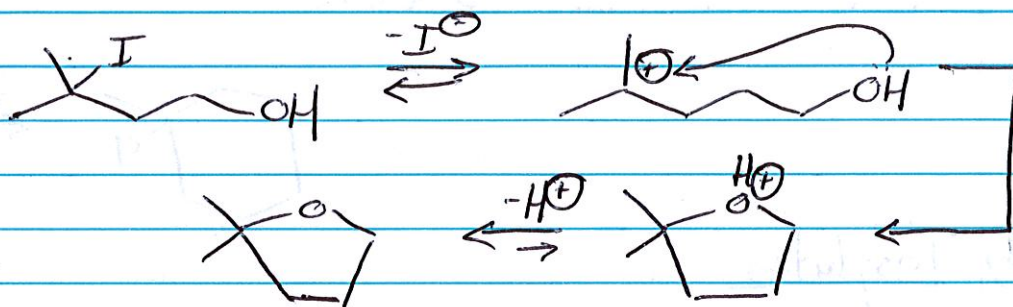
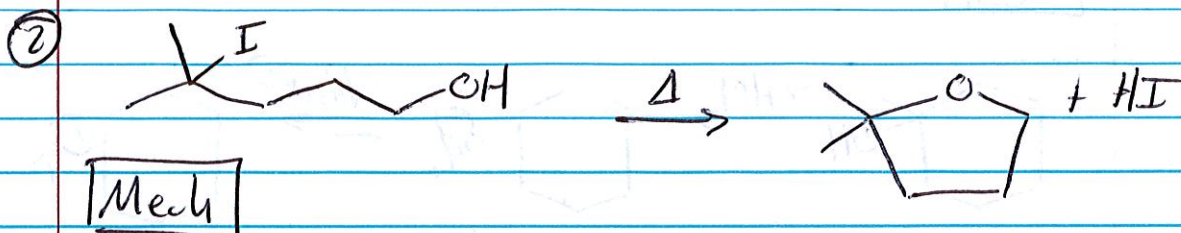
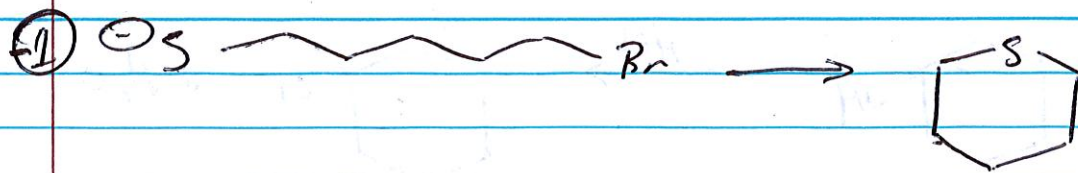


- Example 1



Mech





- alcohols are poor leaving groups.

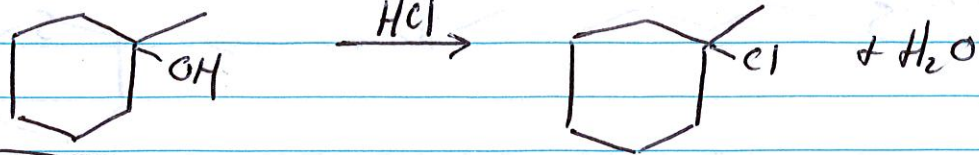


We need these reactions to happen. You can improve the leaving group character of -OH:

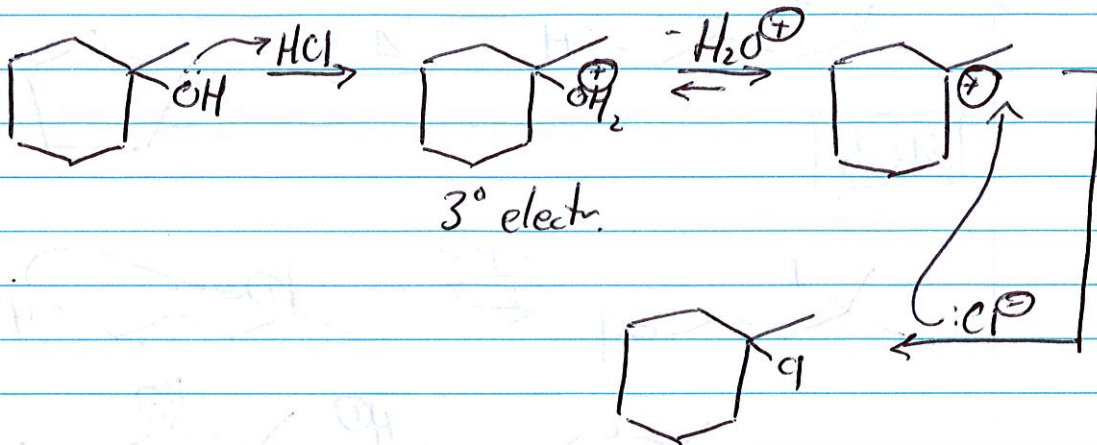
- protonation
- tosylate



②

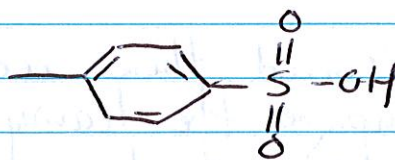
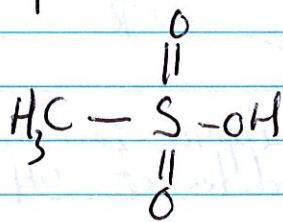


Mech



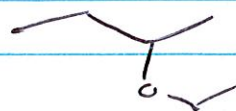
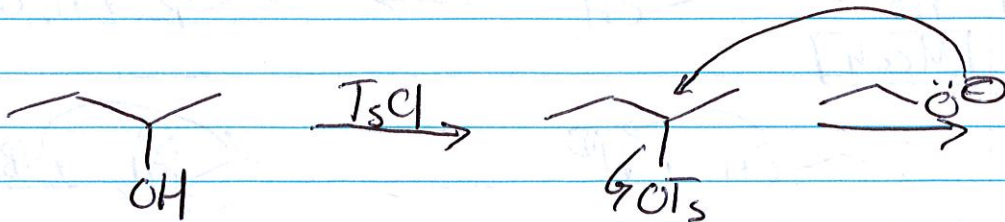
b) Tosylates

Sulfonic acids such as methanesulfonic acid and p-toluenesulfonic acid are strong acids, comparable in acidity with sulfuric acid.



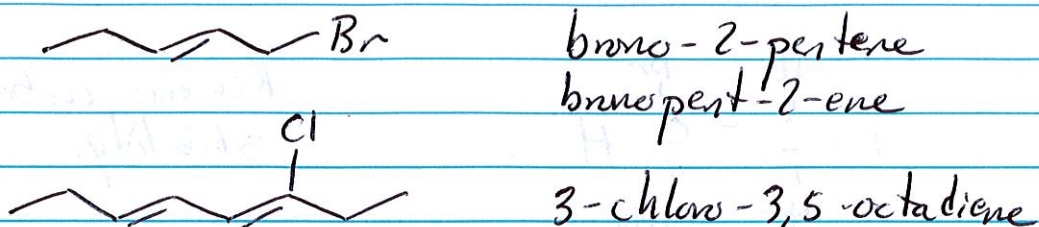
The sulfonates used most frequently are the p-toluenesulfonates.

①



## II. Alkene Chemistry

### Review of Alkene Nomenclature



Alkene mechanisms are even more diverse than substitution reactions. For clarity sake, these <sup>reactions</sup> mechanisms will be organized based on their mechanistic similarities.

Go to

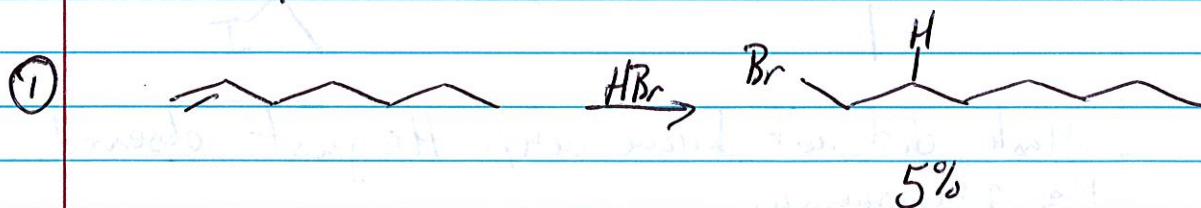
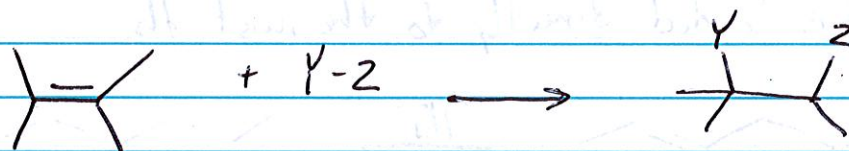
A.

B.

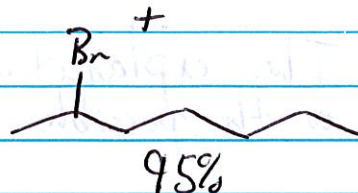
A.

Addition of HX and H<sub>2</sub>O

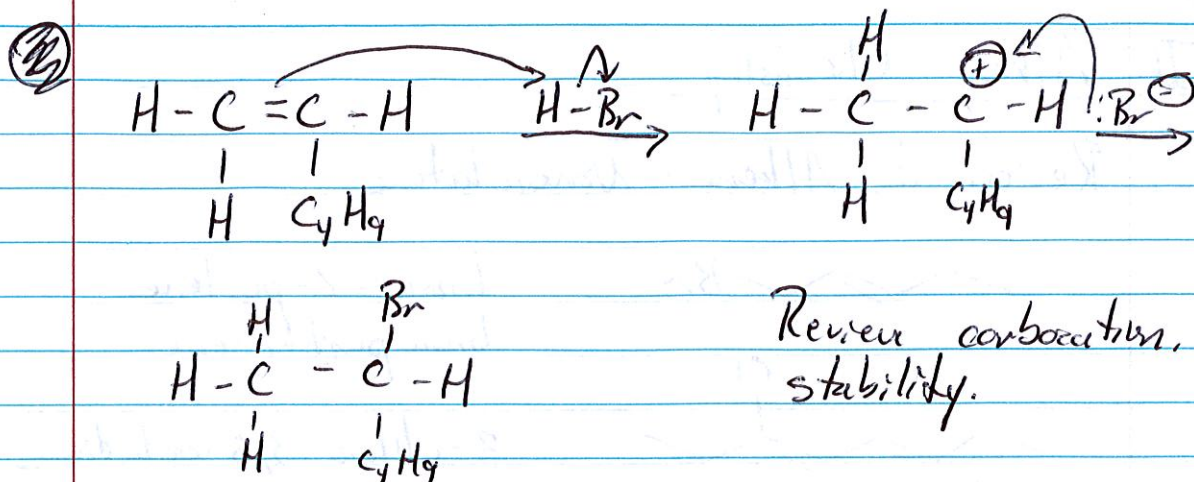
Preparation of Alkenes



Mechanisms are only hypotheses. They are strong hypotheses but remain in the realm of theory.



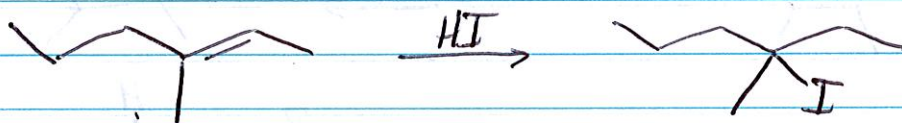
- polarity of bonds is important.  $\delta^+/\delta^-$  can be used to move  $e^-$ s in ways that make chemical sense.



How are the major and minor products determined for these additions?

- 1869, Markovnikov's Rule:

The major product of the rxn has the H of the HX bonded to the carbon of the C=C that is bonded directly to the most Hs.



- Mark did not know why. He just observed the phenomenon.
- The explanation has to do with the stability of the possible carbocations.
- The more carbons attached to the carbocation the more stable it is.  
tertiary > secondary > primary
- Rule: the rich get richer. The poor of the realm is Hydrogens.



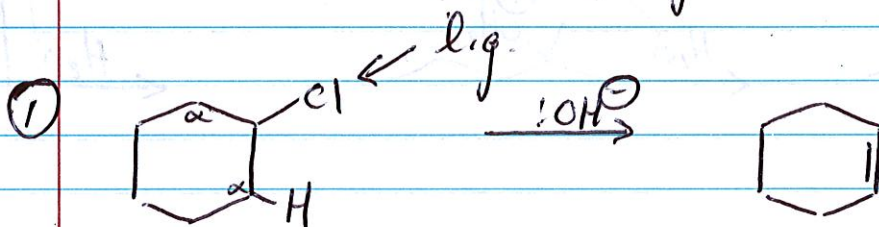
## A. Preparation of Alkenes

- Alkenes are produced through elimination reactions. There are two flavors of elimination reactions: E1 and E2.

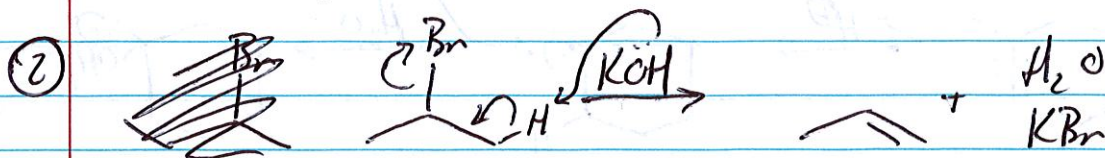
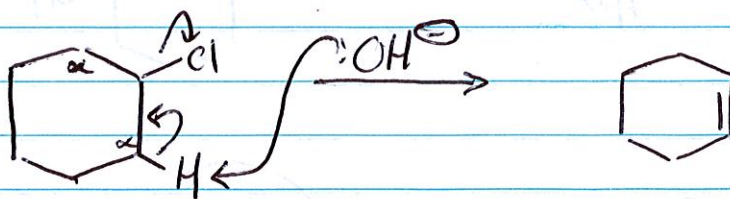
### - E2 Rxns

- elimination bimolecular
- these rxns have some of the same hallmarks of S<sub>N</sub>2 reactions. Nuc. + Electrophile (w/ l.g.)

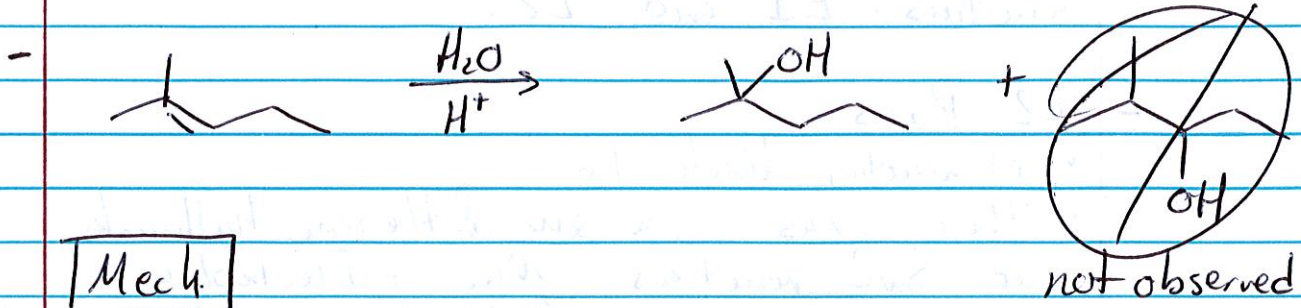
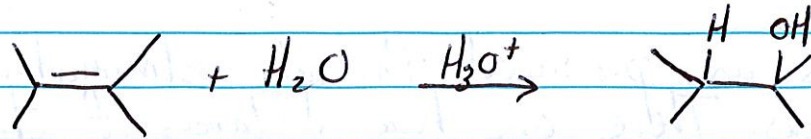
- the elimination refers to the elimination of a hydrogen from an alpha carbon. (aka an alpha hydrogen).



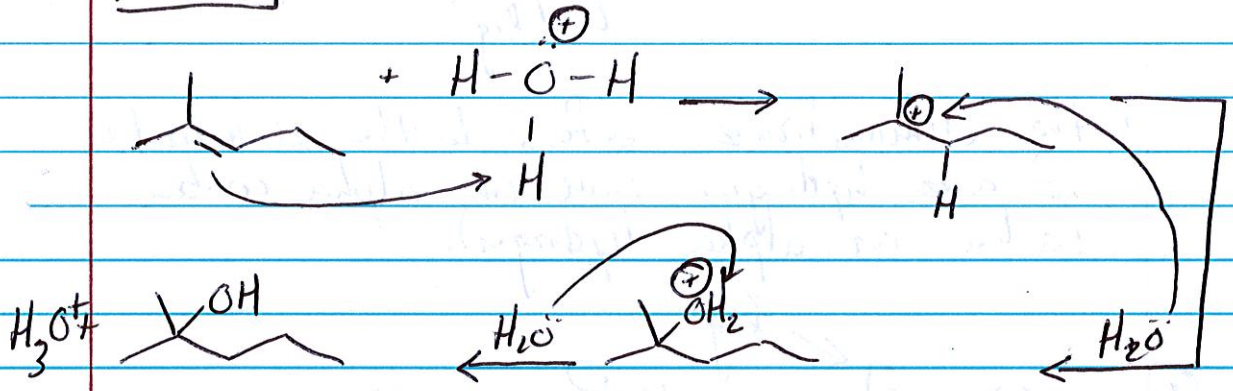
Mech



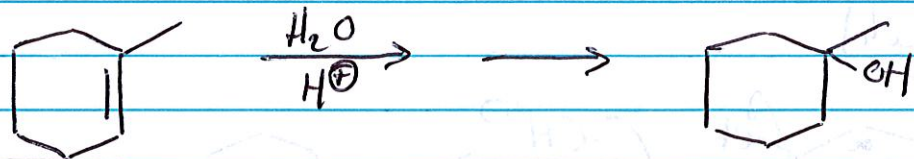
② Addition of H<sub>2</sub>O



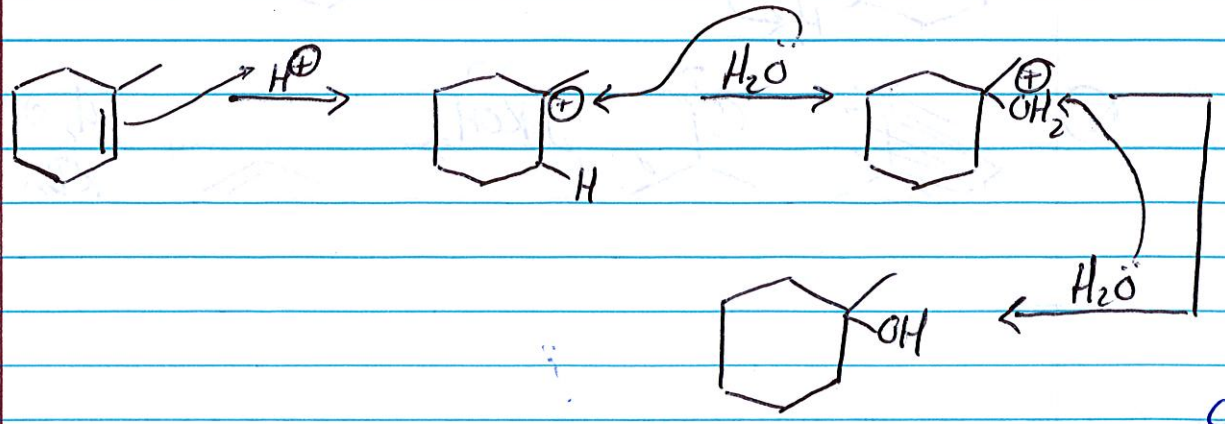
Mech.



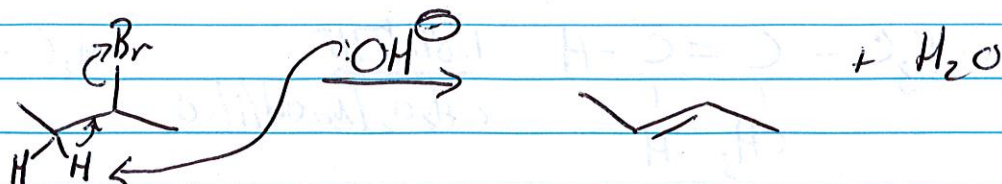
Examples



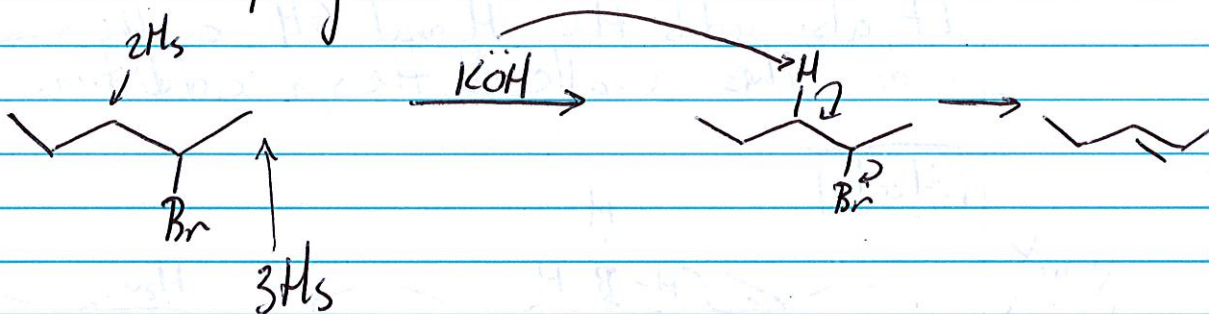
Mech



- we've looked now at compounds which have only one type of  $\alpha$ -H. What happens if there are multiple  $\alpha$  carbons who are identical?



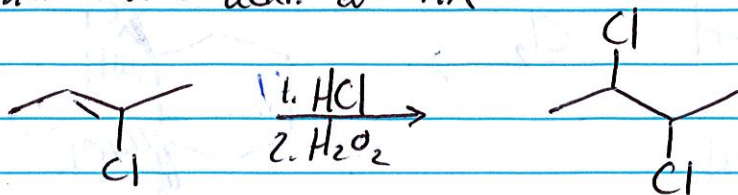
Rule: Be Anti-Robin Hood! Steal from the poor. The coin of the realm, ~~again~~ is Hydrogen.



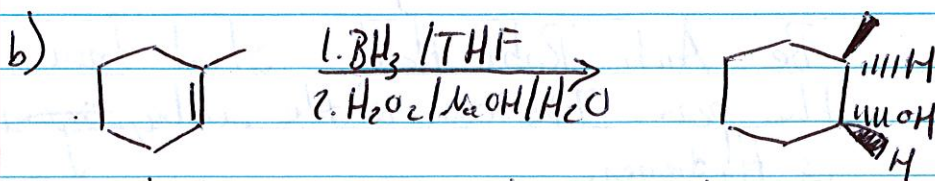
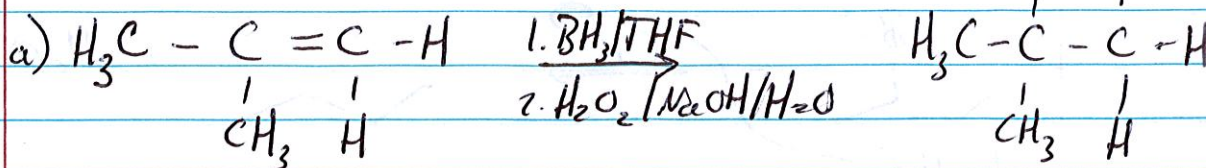
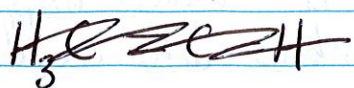
### C. Anti-Markovnikov addition of HX and $\text{H}_2\text{O}$

- In certain ~~and~~ situations we need the halogen and OH group to add in an anti-mark fashion. In most instances, we will use a peroxide ( $\text{ROOR}'$ ) to obtain the anti-mark addition. Mostly  $\text{H}_2\text{O}_2$ .

#### ① Anti-Mark add. of HX



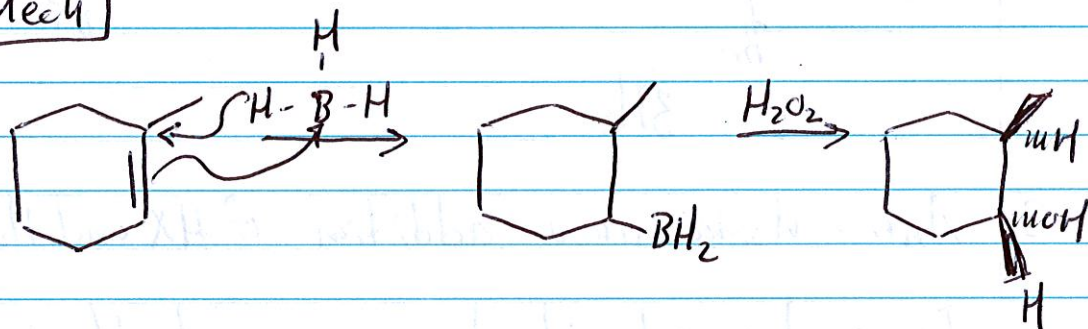
② Anti-mark add. of H<sub>2</sub>O



It also adds the H and OH on the same side. This is called ~~the~~ the syn addition.

Mech

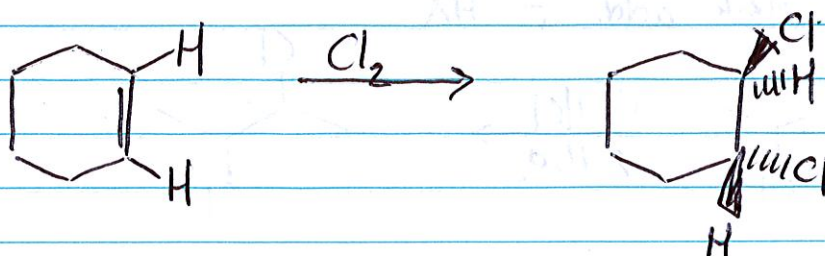
Will not be tested.



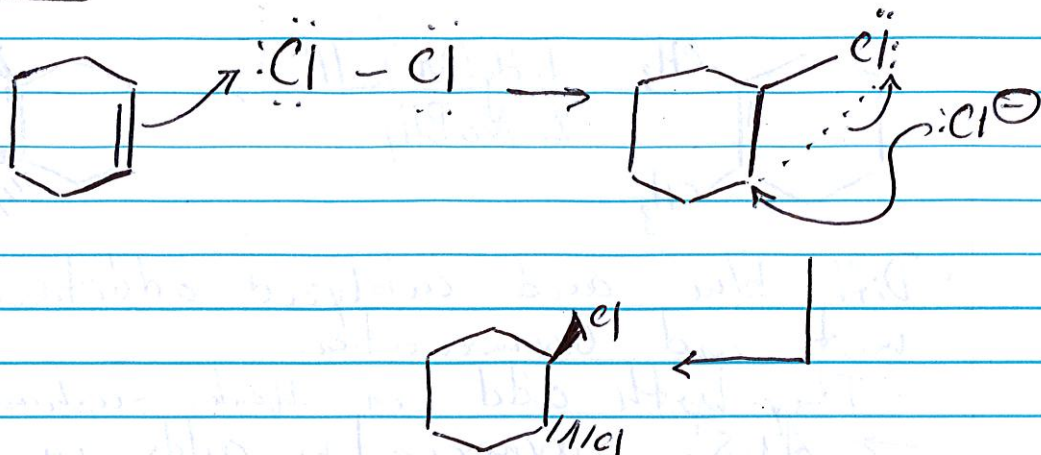
D. Addition of Halogens, Epoxidation, Oxymercuration

① Add. of X<sub>2</sub>

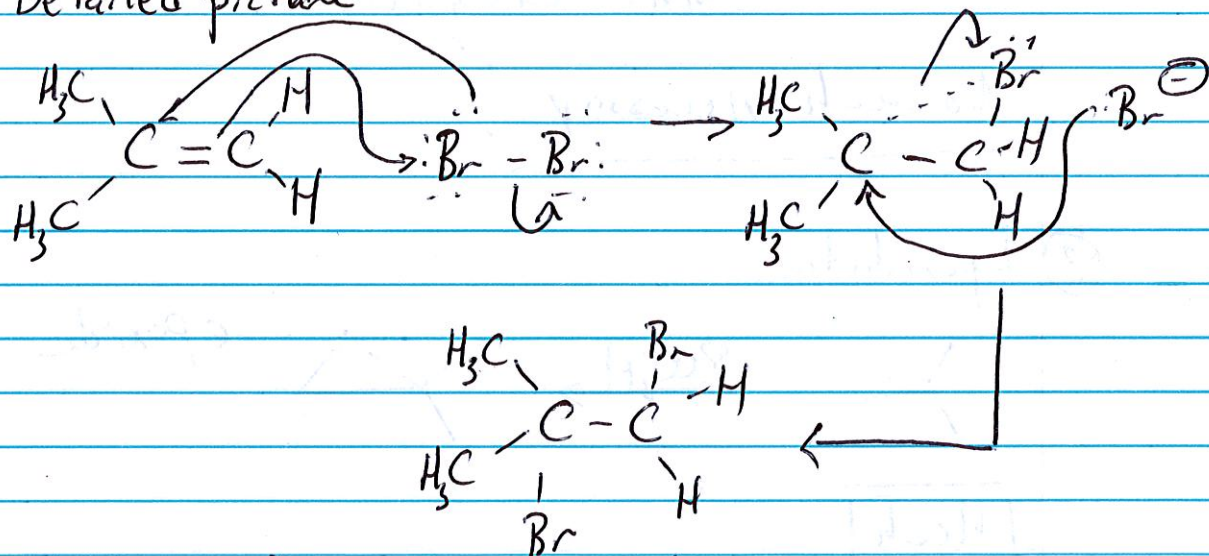
→ adds in an anti addition (discuss diff b/w "anti" and "anti-mark")



Mech

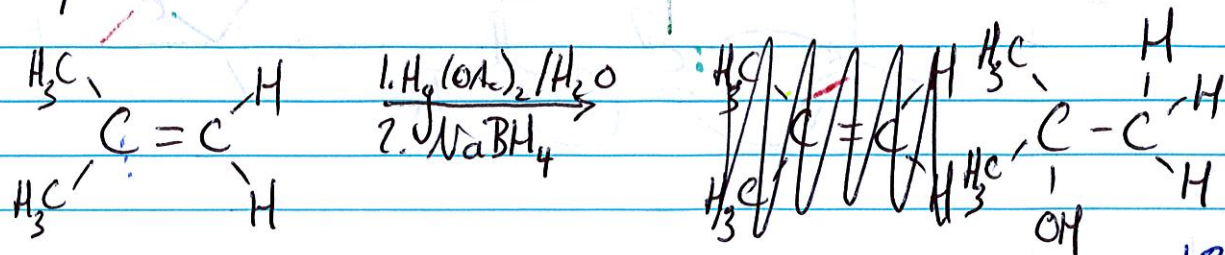


Detailed picture

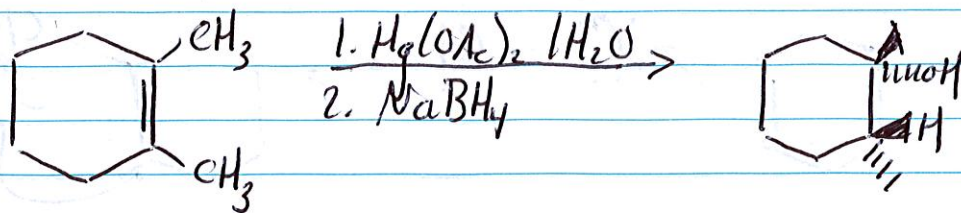


Treatment of a dil. soln of  $\text{Br}_2$  is a qual. test for a  $\text{C}=\text{C}$  or  $\text{C}\equiv\text{C}$  because the red-orange color disappears after each drop of  $\text{Br}_2$  solution.

② Oxymercuration



② (cont.)



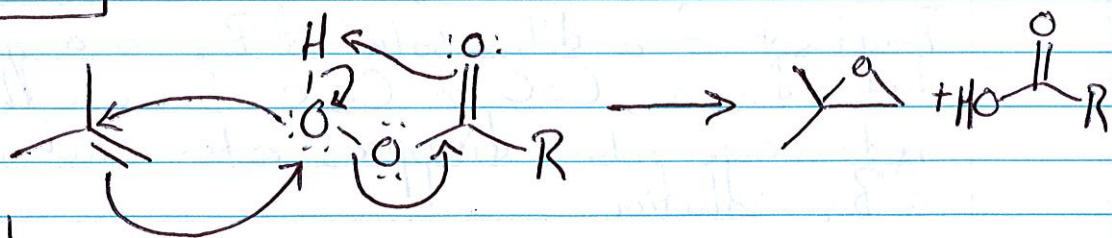
- Diff. but acid catalyzed addition of water and oxymercuration.
- They both add in Mark. fashion
- ANS: oxymercuration adds in anti. configuration.

No mech necessary!

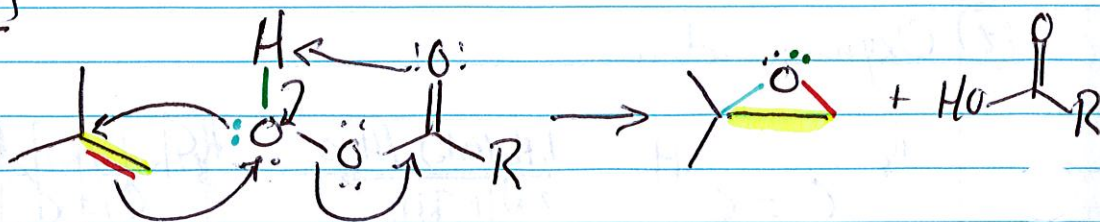
③ Epoxidation



Mech

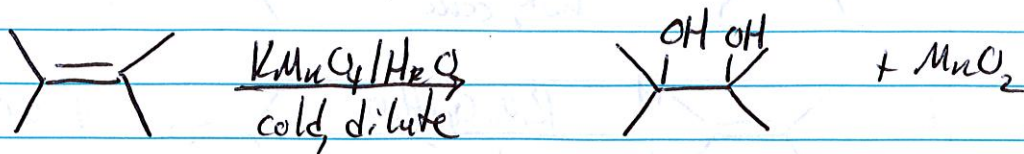


Color Mech

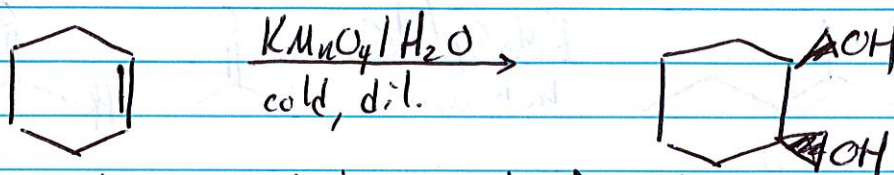
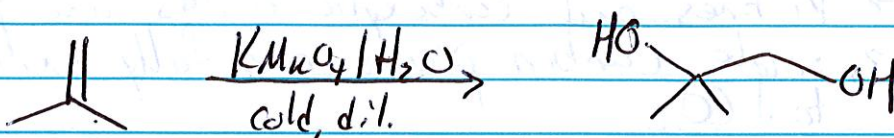


## E. Oxidation of Alkenes ( $O_3 / KMnO_4$ )

① cold dilute  $KMnO_4 / H_2O$

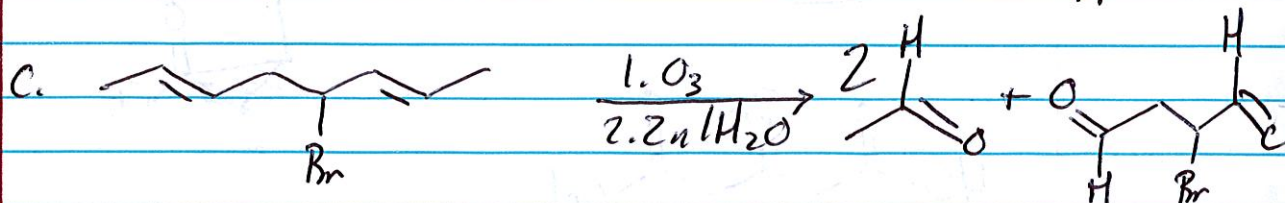
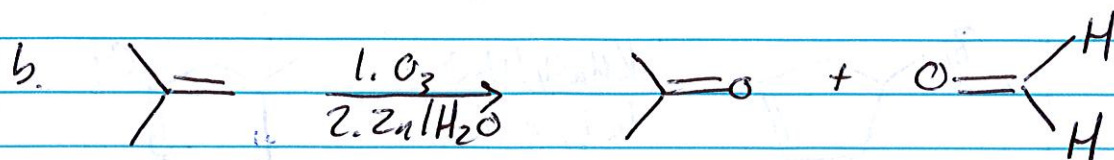
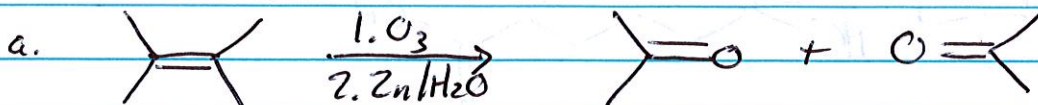


②

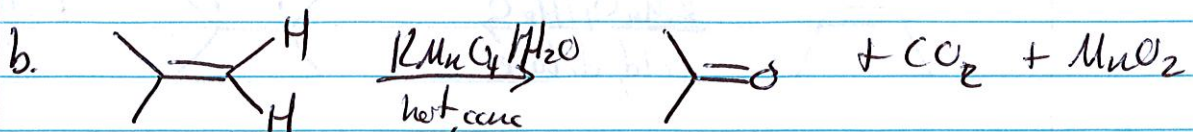
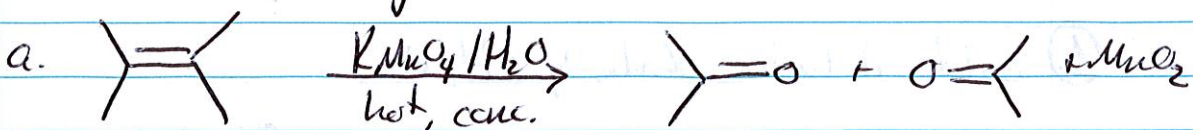


→ simple qualitative test for the presence of double or triple bonds because of the color change.  
 $MnO_4^-$  (purple)  $\longrightarrow$   $MnO_2$  (black-brown).

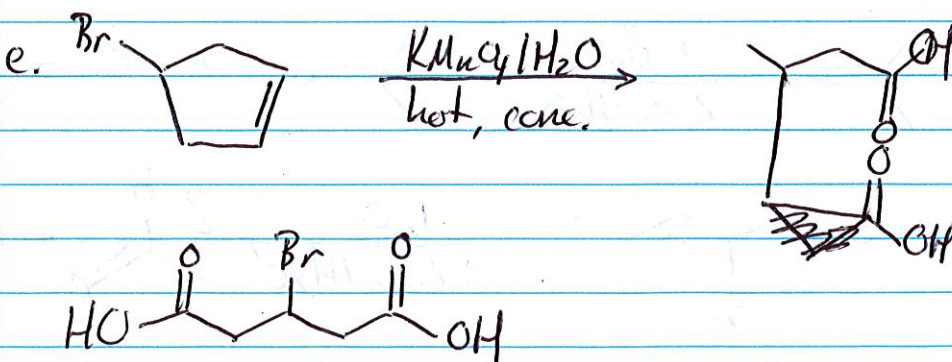
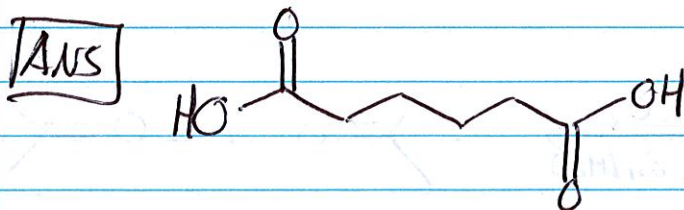
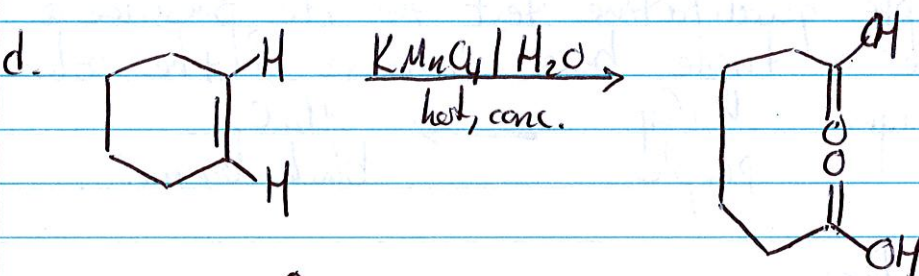
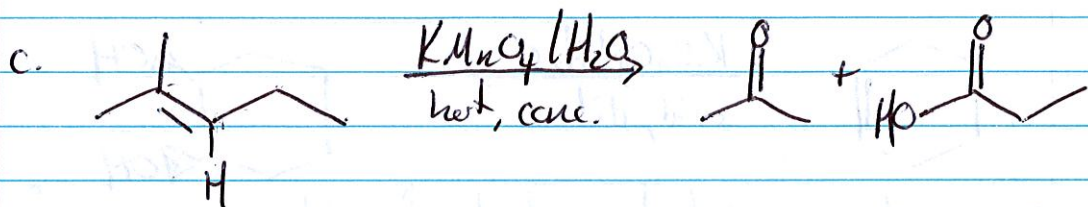
② Ozonolysis



③ oxidative cleavage

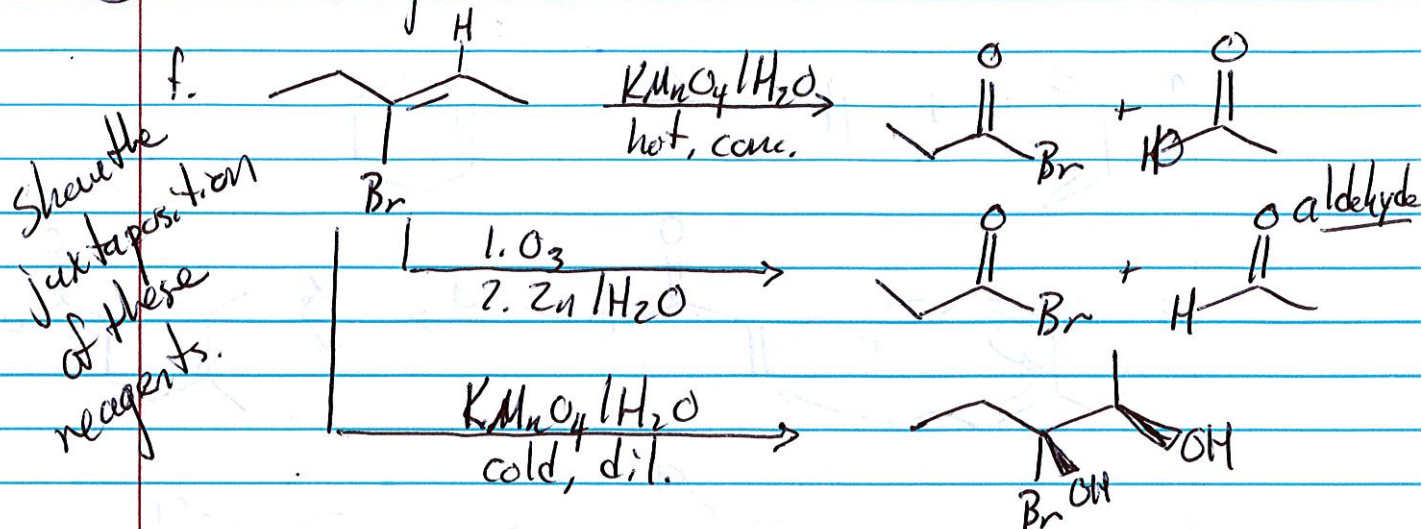


→ ketones and carboxylic acids are products  
→ single carbon pieces are fully oxidized to CO<sub>2</sub>



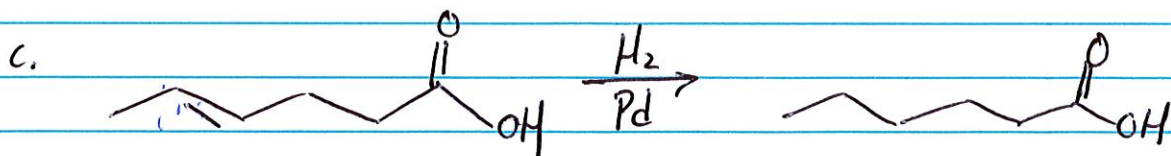
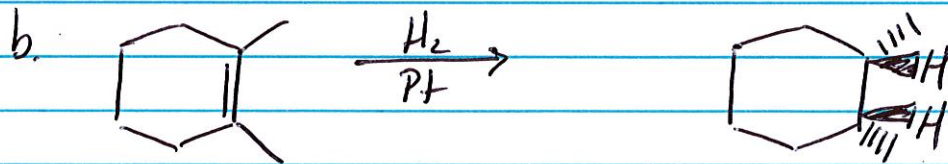
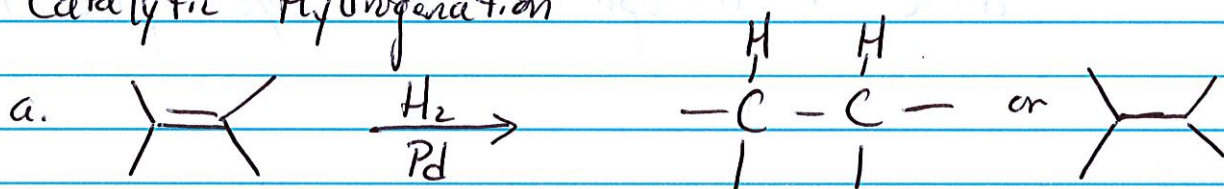


### ③ Ox. cleavage (cont.)



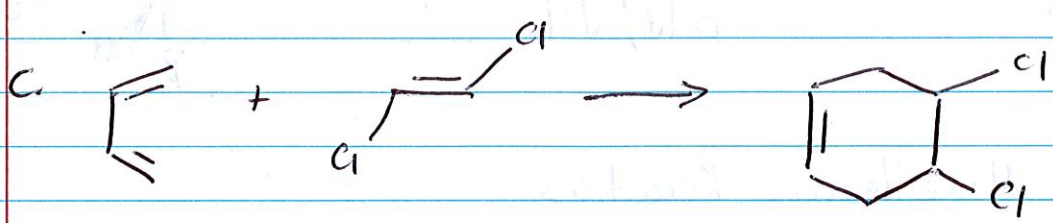
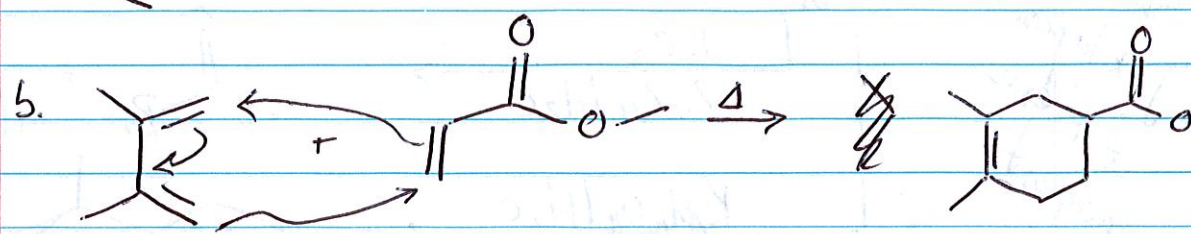
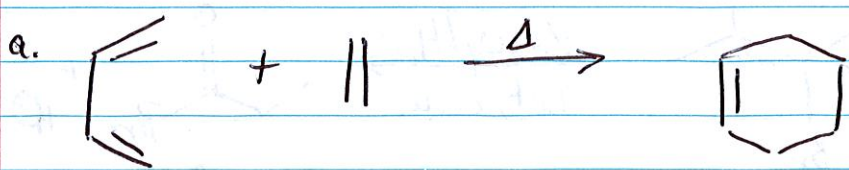
### F. Miscellaneous Reactions

#### ① Catalytic Hydrogenation



The only functional group that is hydrogenated is the alkene. No carbonyl groups or benzene/phenyl groups

## ② Diels-Alder Reaction



diene + dienophile  $\rightarrow$  cyclic product.