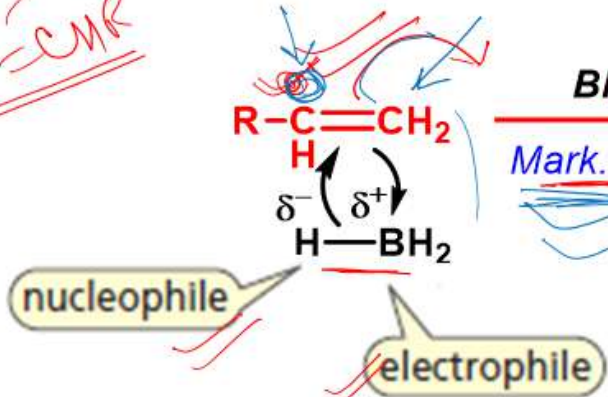
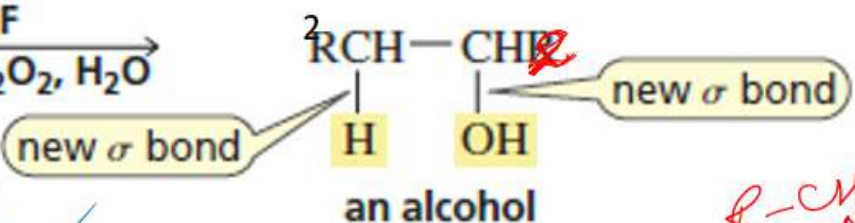
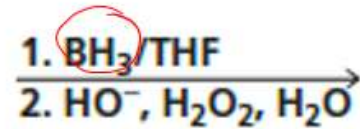
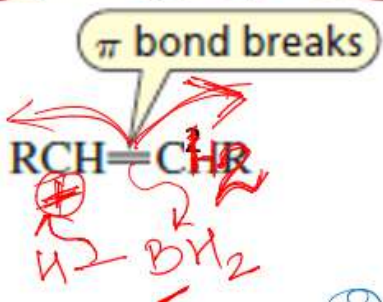


# Hydroboration-Oxidation

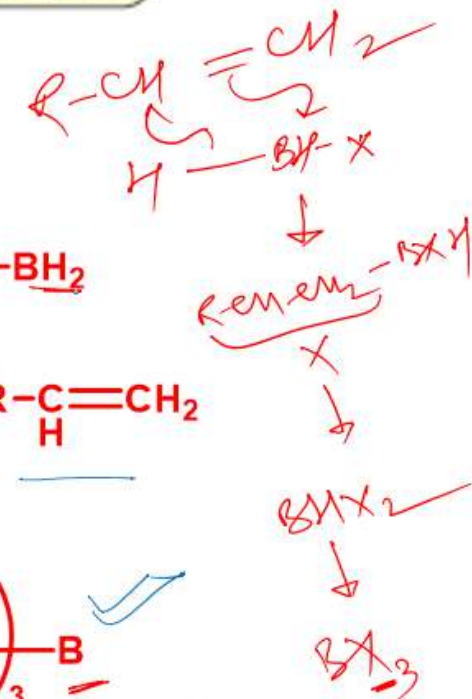
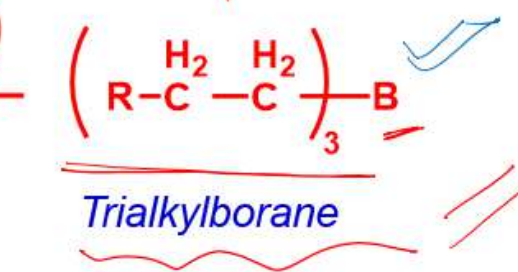
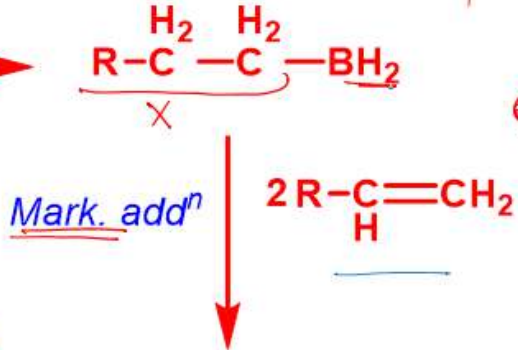
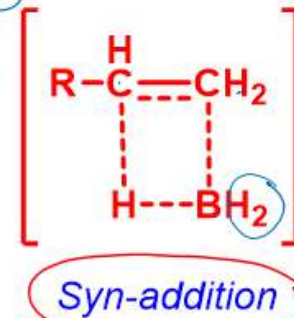
① Starting - M.K.  
 ② Product - Anti-M.K.  
 ③ Syn-addition

## MECHANISM:

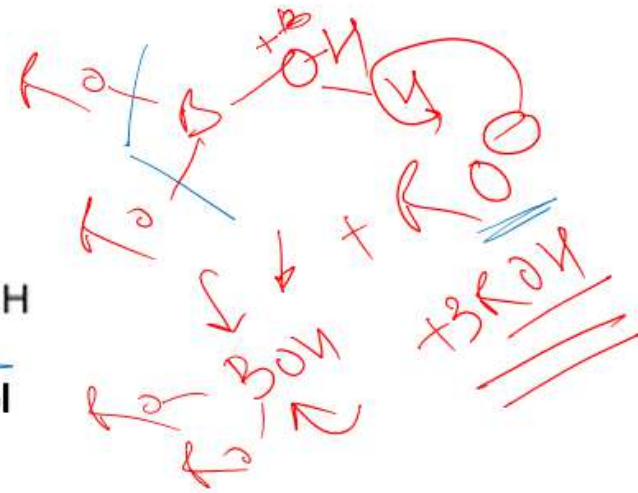
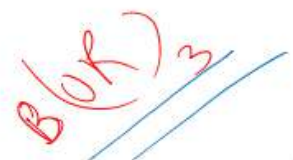
$RCH=CH_2$



$R-CH=CH_2$   
 $H-BH_2$

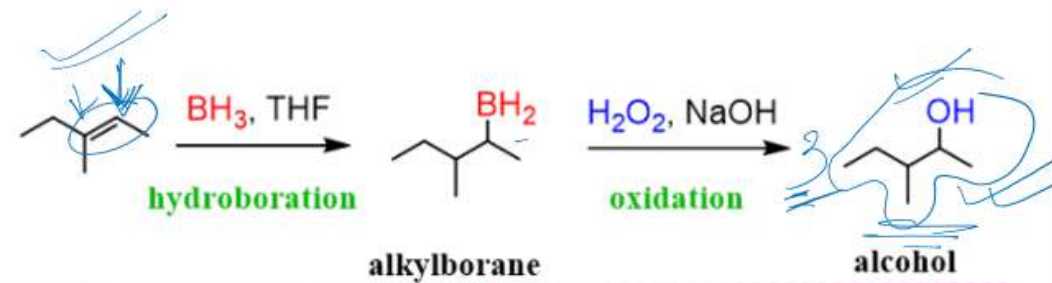
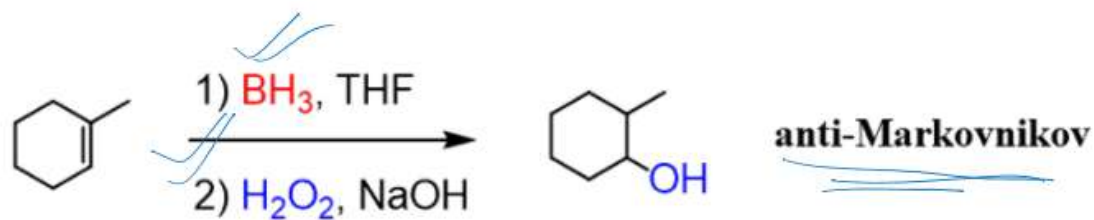
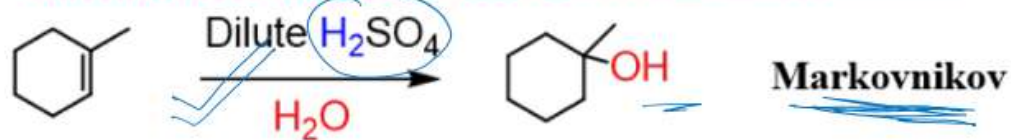
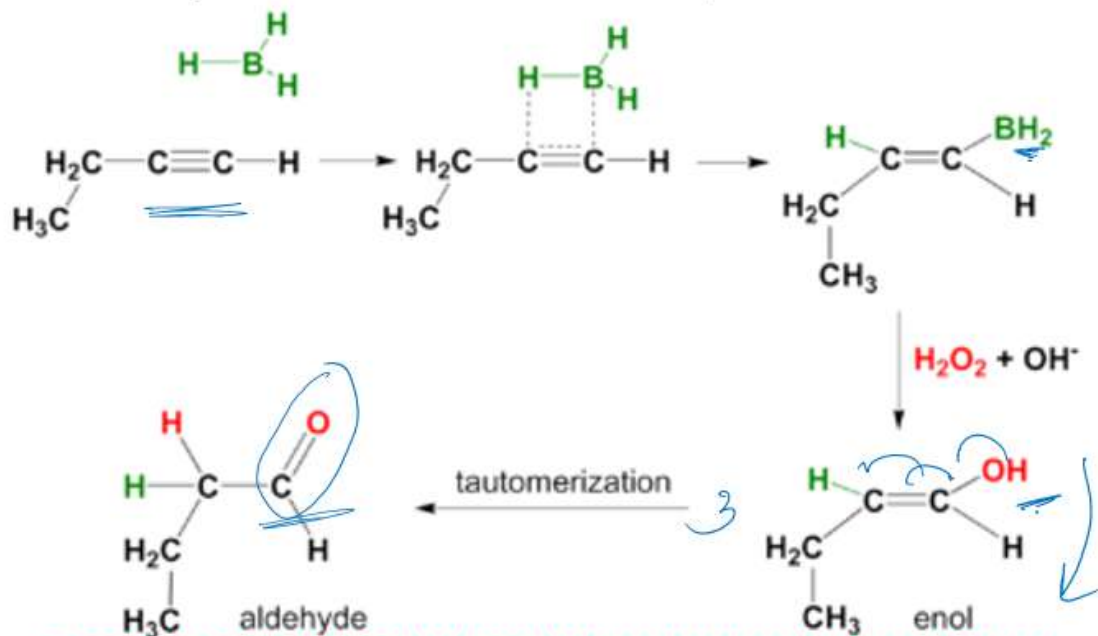


$\delta^-$   
 $H-BH_2$   
 Hybrid

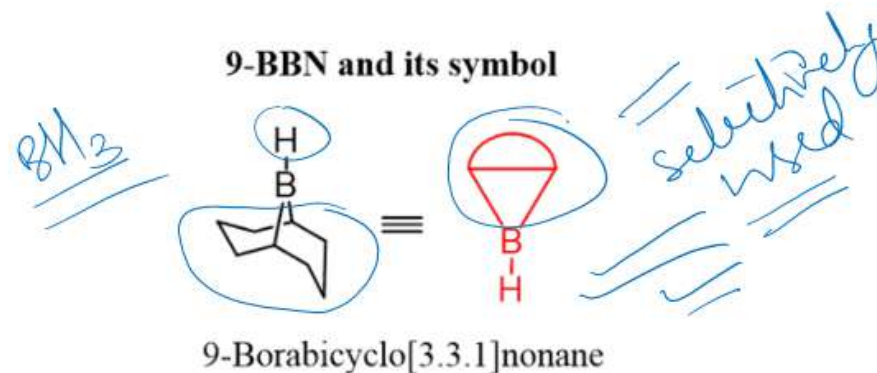


## EXAMPLES:

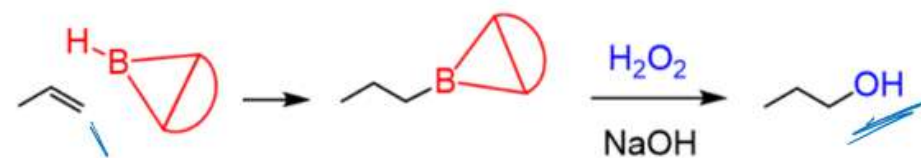
### Hydroboration-oxidation in Alkyne



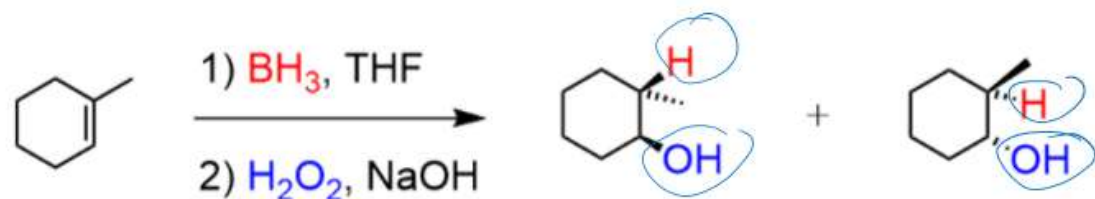
### 9-BBN and its symbol



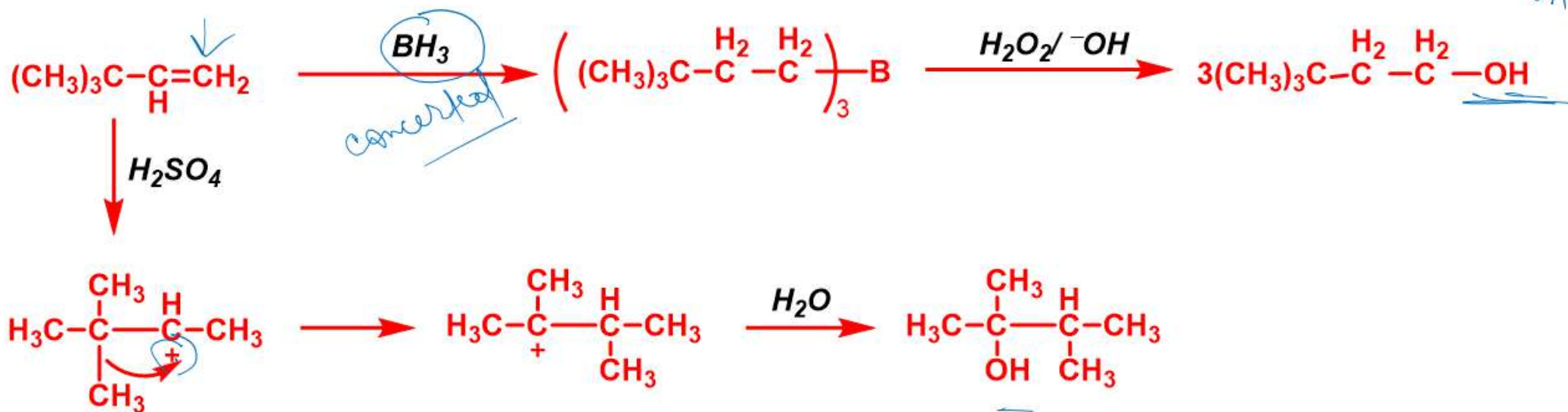
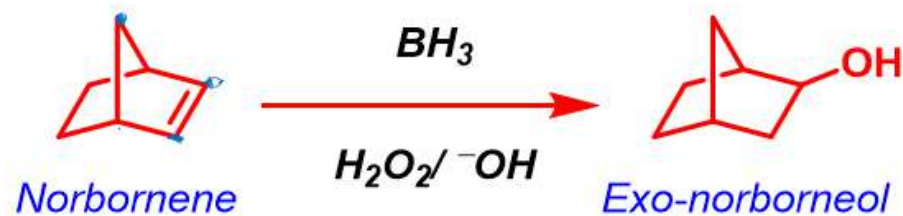
As an example:

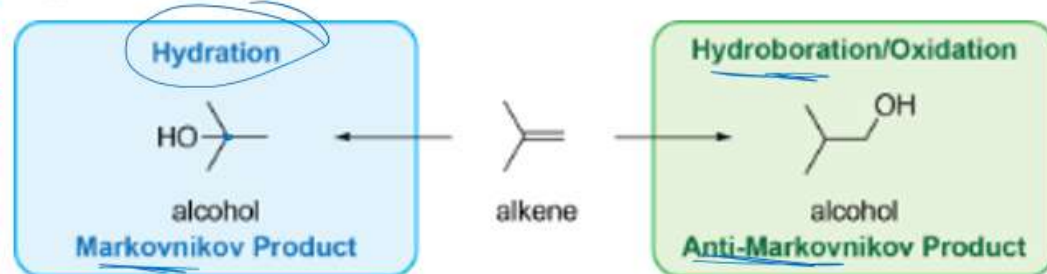
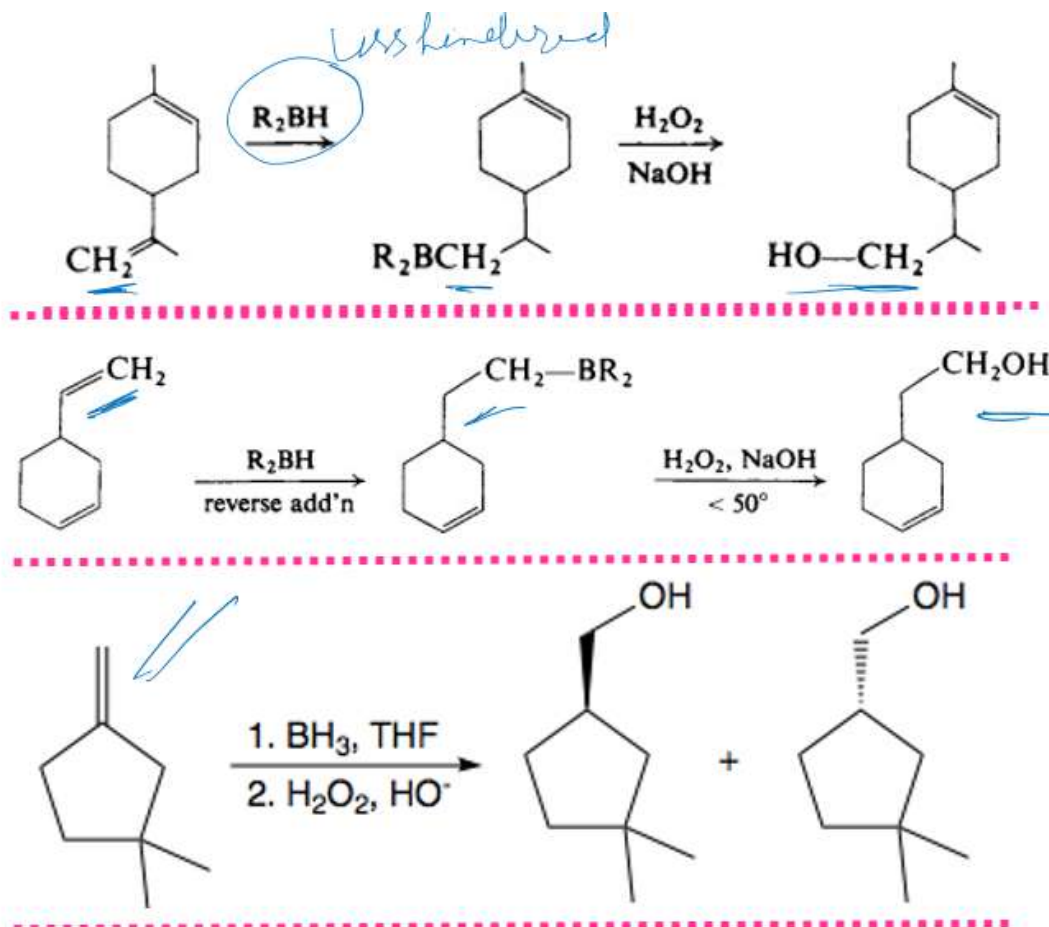
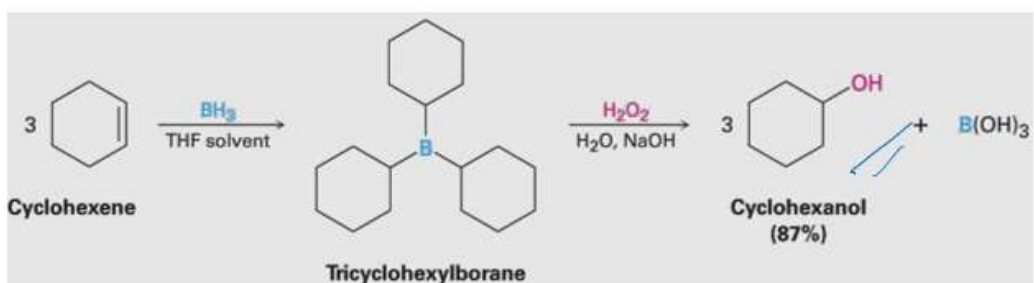
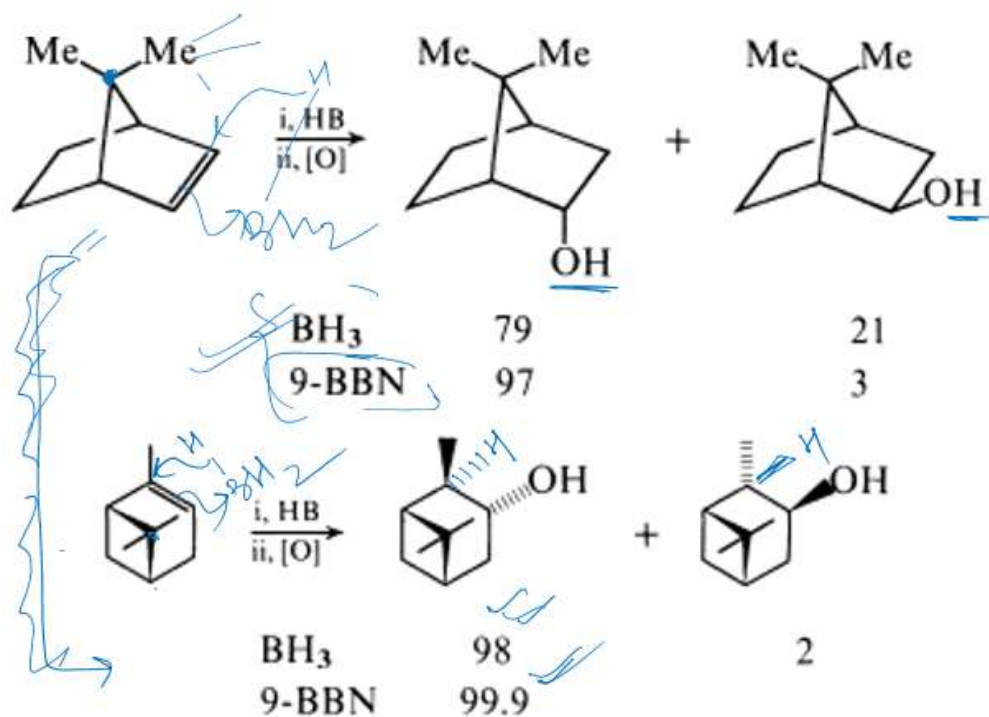


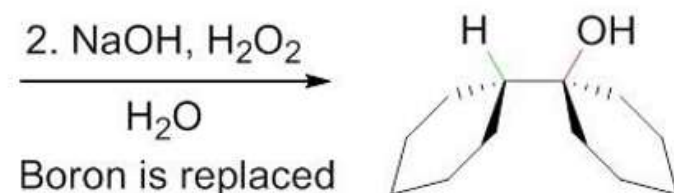
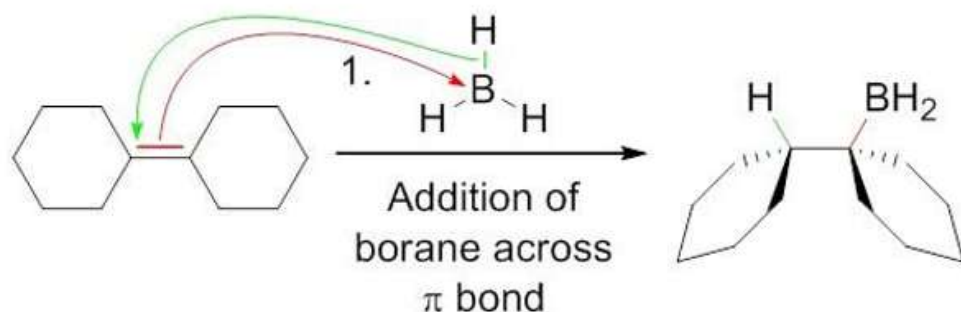




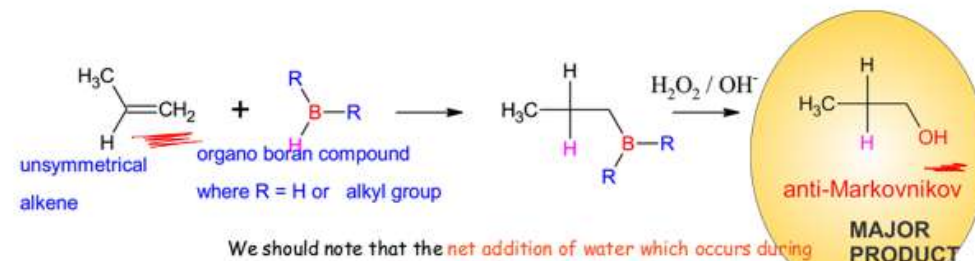
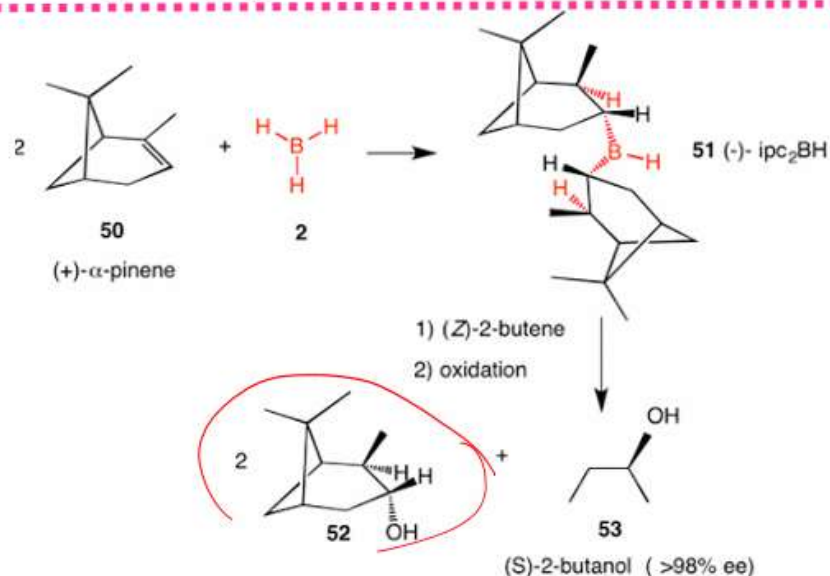
Enantiomers  
syn addition







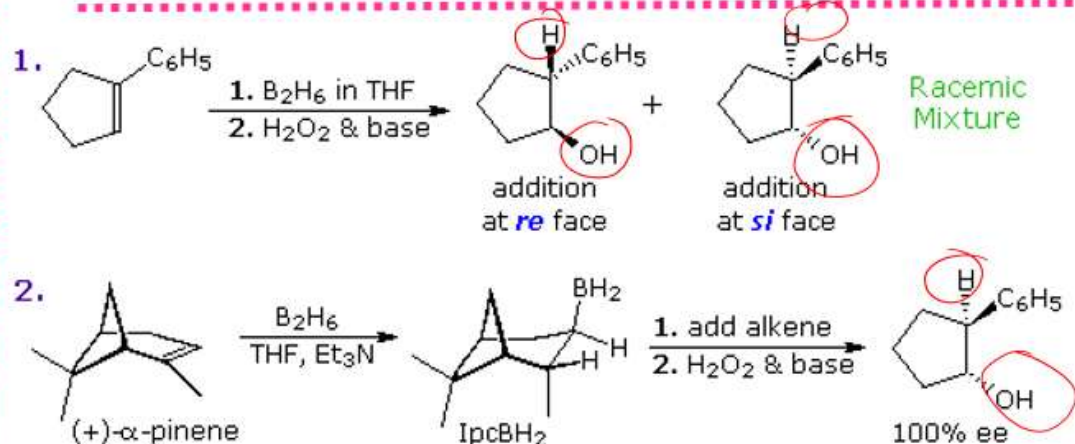
Boron is replaced where it stands by a hydroxyl group

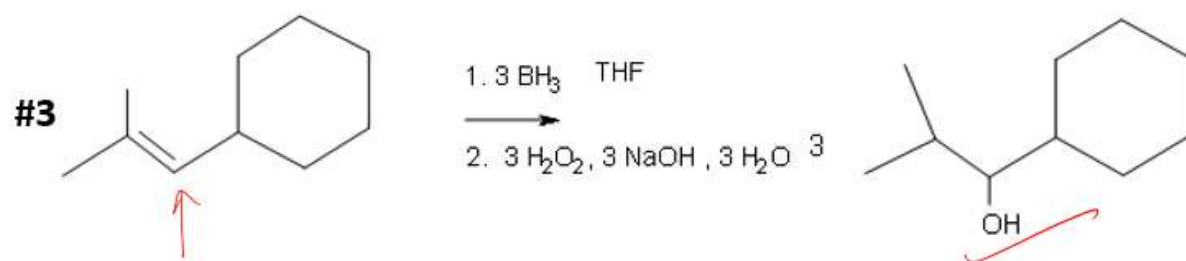


We should note that the net addition of water which occurs during hydroboration/oxidation is in the anti-Markovnikov regiochemical sense, with propene giving 1-propanol, rather than the 2-propanol which is generated by the acid catalyzed, electrophilic hydration mechanism.



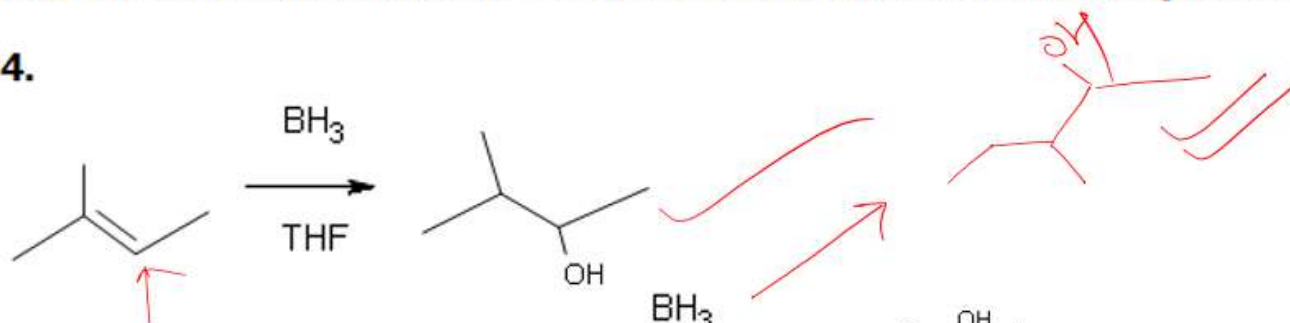
NOTE : what was anti markovnikov minor hydration product in normal acidic addition is a major product in HYDROBORATION



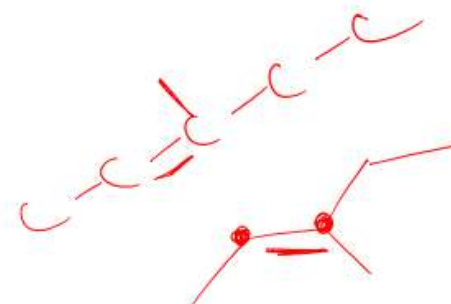
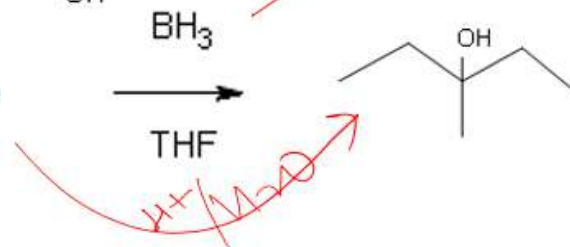


Draw the structural formulas for the alcohols that result from hydroboration-oxidation of the alkenes shown.

#4.



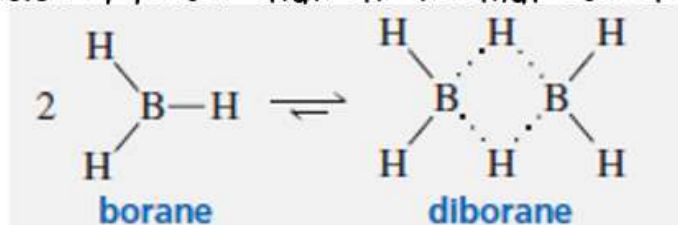
#5. (E)-3-methyl-2-pentene



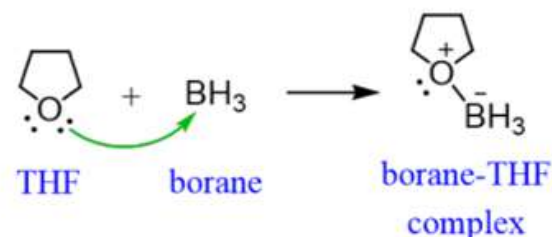
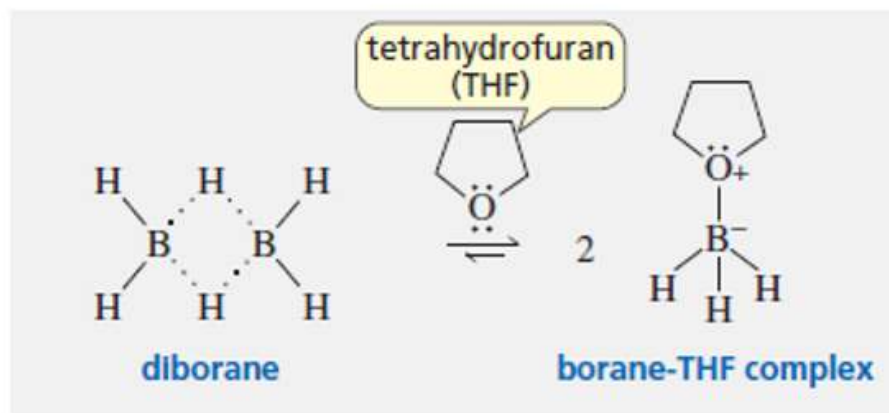


## Note:

- Borane exists primarily as a colorless gas called diborane. Diborane is a **dimer**—a molecule formed by joining two identical molecules. Because boron does not have a complete octet—it is surrounded by only six electrons—it has a strong tendency to acquire an additional electron pair. In the dimer, therefore, two boron atoms share the two electrons in a hydrogen–boron bond by means of unusual half-bonds. These hydrogen–boron bonds are shown as dotted lines to indicate that they consist of fewer than the normal two electrons.



- Diborane ( $\text{B}_2\text{H}_6$ ) is a flammable, toxic, and explosive gas. A complex—prepared by dissolving diborane in THF—is a more convenient and less dangerous reagent. One of the lone pairs of the O atom in THF provides the two electrons that boron needs to complete its octet. The borane–THF complex is used as the source of  $\text{BH}_3$  for hydroboration.
- THF (tetrahydrofuran) is the solvent that is used to stabilize the dimer of  $\text{BH}_3$  which is a flammable, toxic, and explosive gas:





# Oxymercuration-Demercuration

Alkene react with mercuric acetate ( $\text{Hg}^{2+}$  salt) and an oxygen nucleophile (water or an alcohol) in the presence of THF (tetrahydrofuran) as solvent to yield hydroxymercurial compound (Organomercury intermediate). This is known as Oxymercuration reaction.

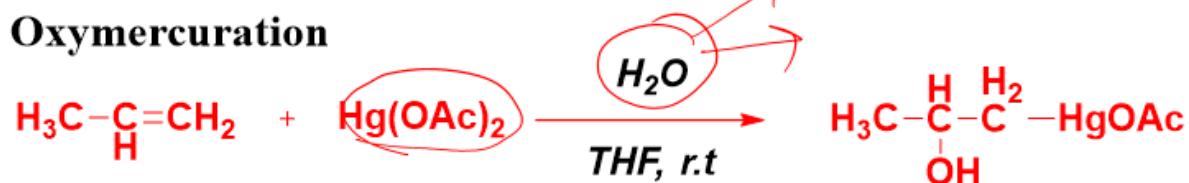
The hydroxymercurial compound on reductive cleavage with  $\text{NaBH}_4$ , results in the formation of alcohol (when the nucleophile is water), or an ether (when the nucleophile is an alcohol) and this process is known as Demercuration.

The overall process is the hydration of alkene in accordance with Markovnikov's rule.

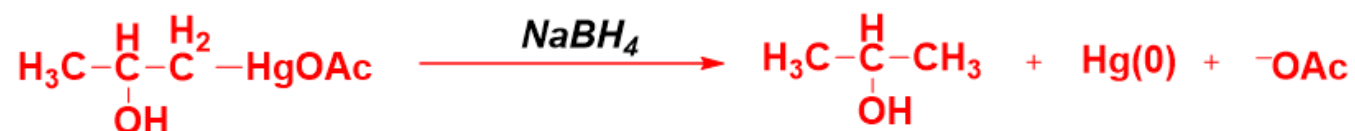
Characteristics of oxymercuration- demercuration are:

- ✓ No rearrangements (no carbocation intermediate, cyclic mercurinium ion is the intermediate)
- Product is analogous to (almost exclusive) Markovnikov addition of water (Regioselectivity predicted by Markovnikov's rule favors most highly substituted alcohol)
- Trans (or anti-addition) of -H and -OH across  $>\text{C}=\text{C}<$

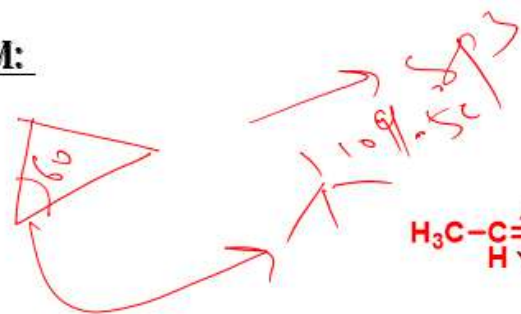
## Step I: Oxymercuration



## Step II: Demercuration



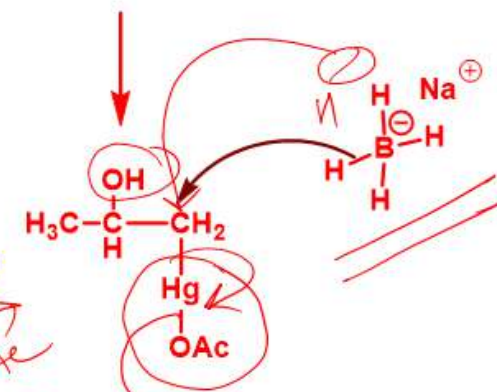
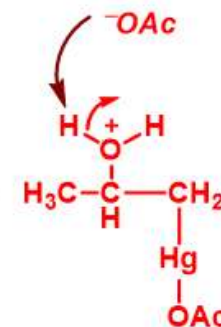
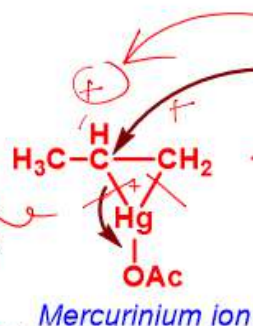
## MECHANISM:



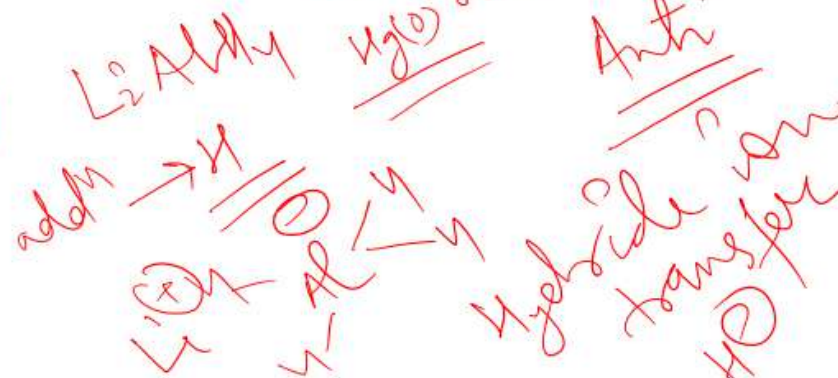
Concerted 1<sup>st</sup> step

*torsional unstable*  
*60° reactive*

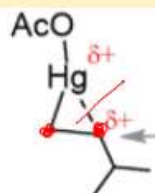
-OAc



2° alcohol  
(Markownikoff addition product)

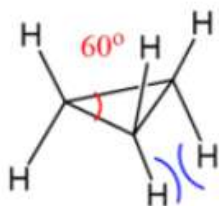


Three-membered rings are not very stable, meaning they are quite reactive. The reason for this is the **ring tension** and the **torsional strain** i.e. carbons are not in optimal geometry as the angle between them is 60° vs 109.5° which is what it should be for sp<sup>3</sup>-hybridized tetrahedral atoms.



Electrophilic center  
Cannot rearrange

Ring tension

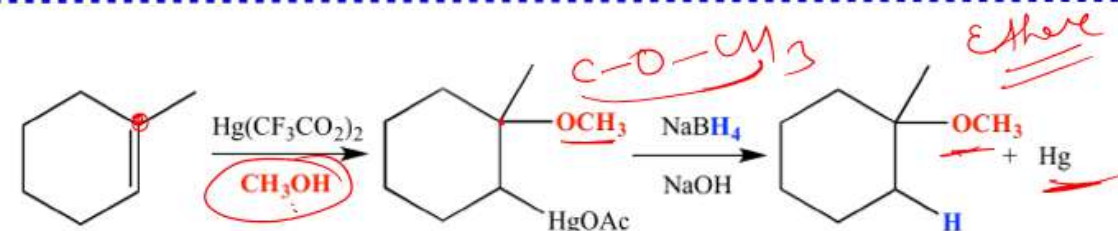
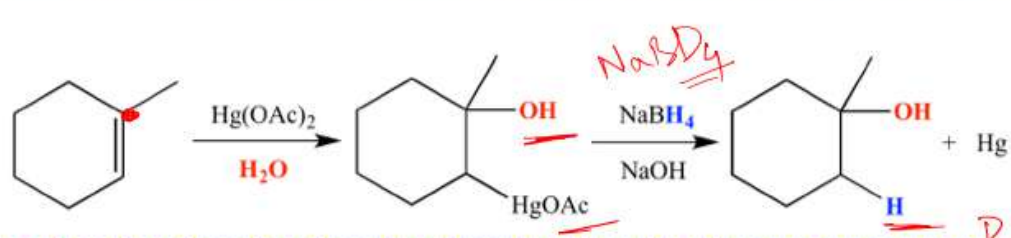
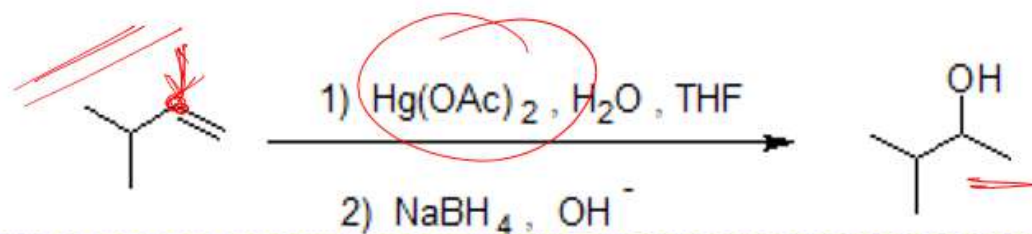
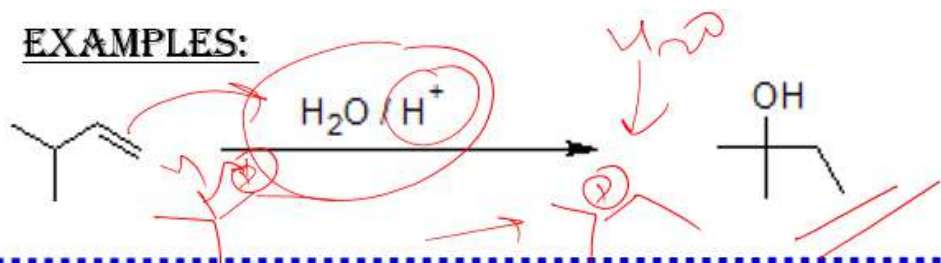


Eclipsing hydrogens -  
high torsional strain

Ring tension,  
reactive

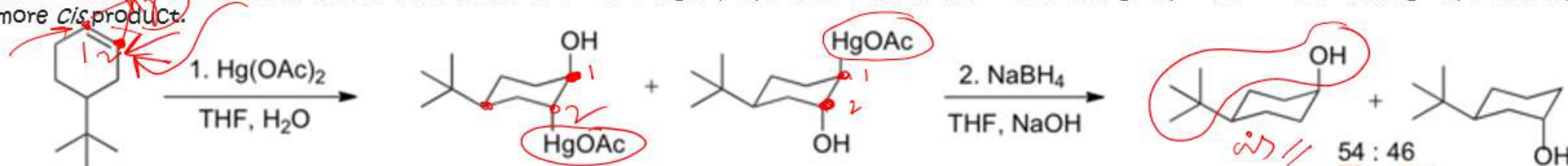


## EXAMPLES:

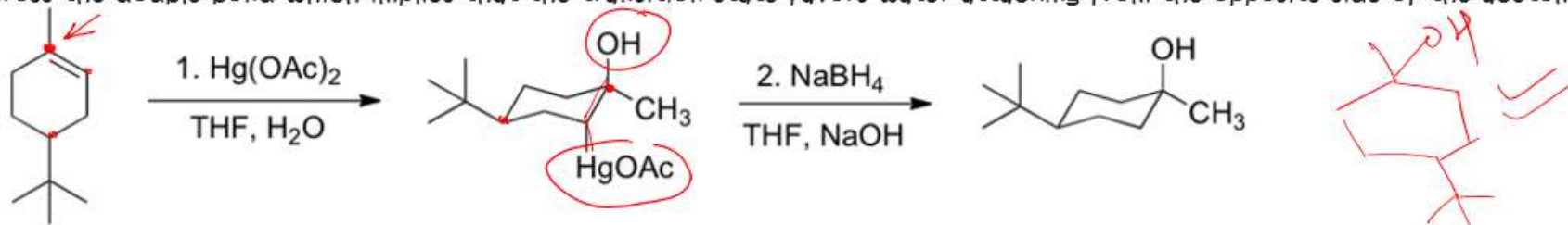


## Regioselectivity and Stereospecificity of the oxymercuration reaction with substituted cyclohexenes:

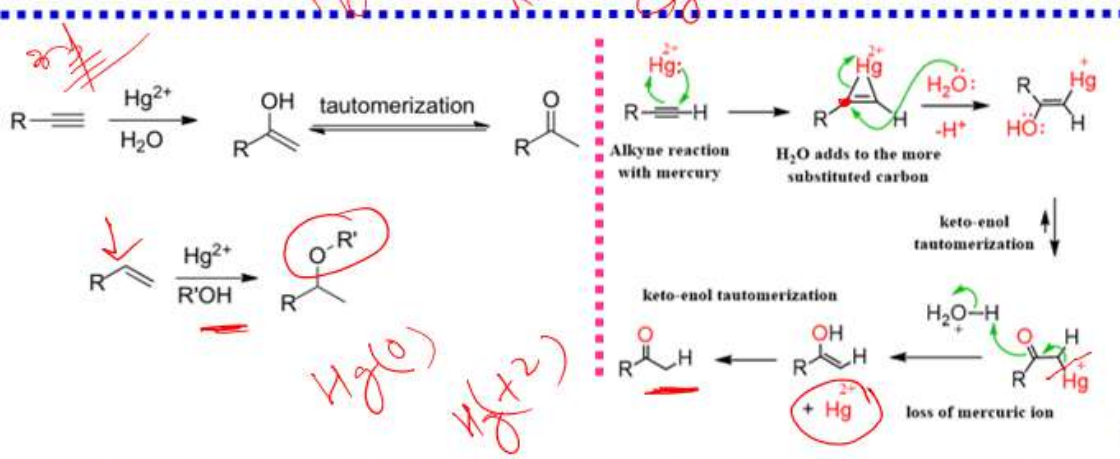
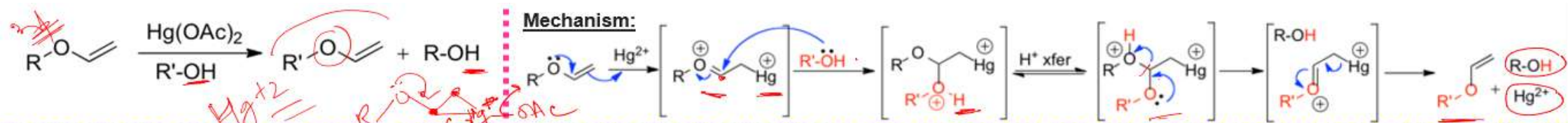
A bulky group like *t*-butyl locks the ring in a **Chair Conformation** and prevents ring flips. With 4-*t*-butylcyclohexene, oxymercuration yields two products – where addition across the double bond is always *anti* – with slight preference towards an acetoxymercury group *trans* to the *t*-butyl group, resulting in slightly more *cis* product.



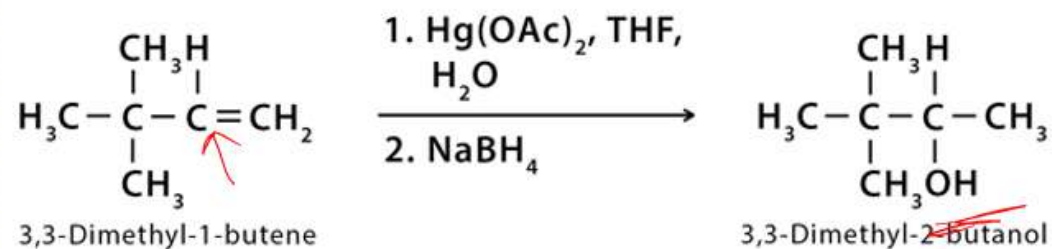
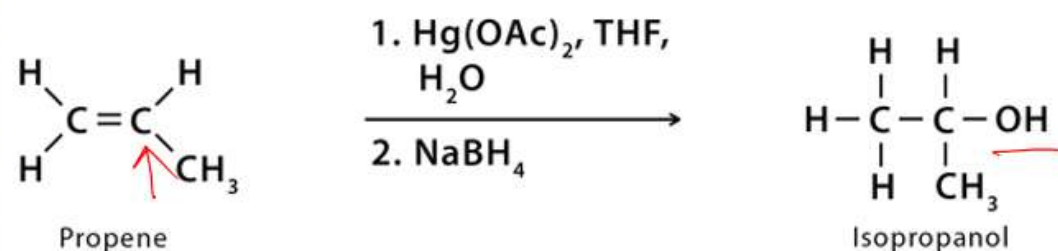
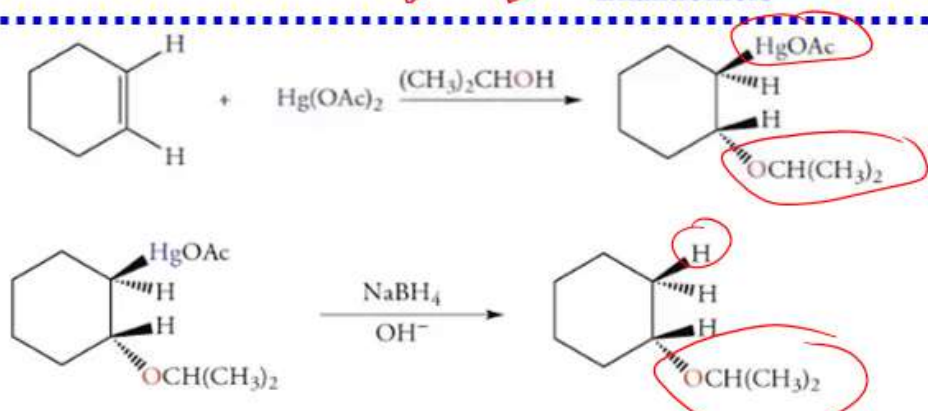
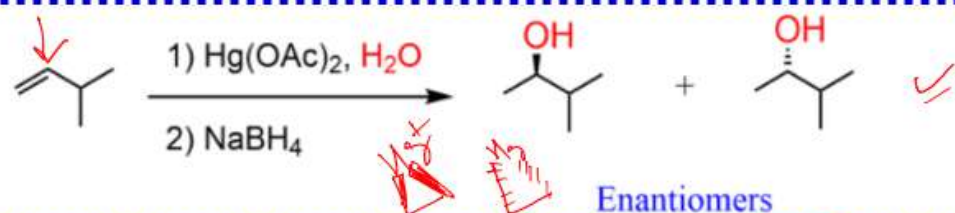
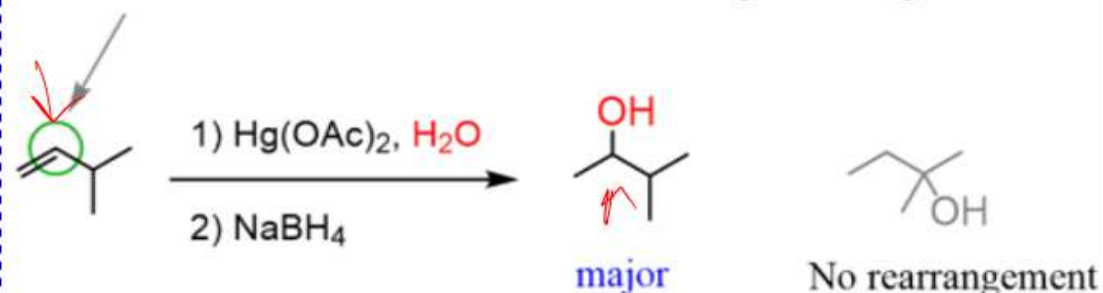
With 1-methyl-4-*t*-butylcyclohexene, oxymercuration yields only one product – still *anti* addition across the double bond – where water only attacks the more substituted carbon. The reason for *anti* addition across the double bond is to maximize orbital overlap of the lone pair of water and the empty orbital of the mercuronium ion on the opposite side of the acetoxymercury group. Regioselectivity is observed to favor water attacking the more substituted carbon, but water does not add *syn* across the double bond which implies that the transition state favors water attacking from the opposite side of the acetoxymercury group.

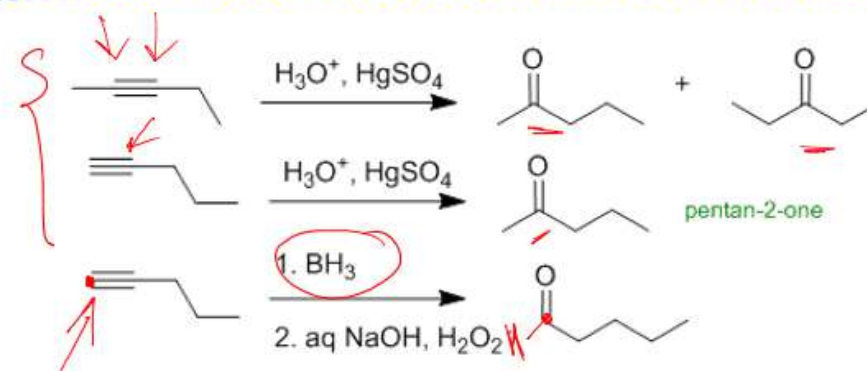
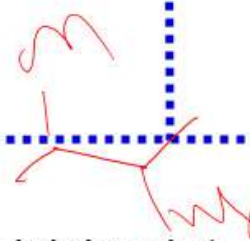
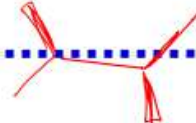
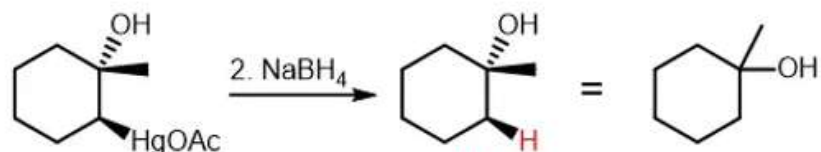
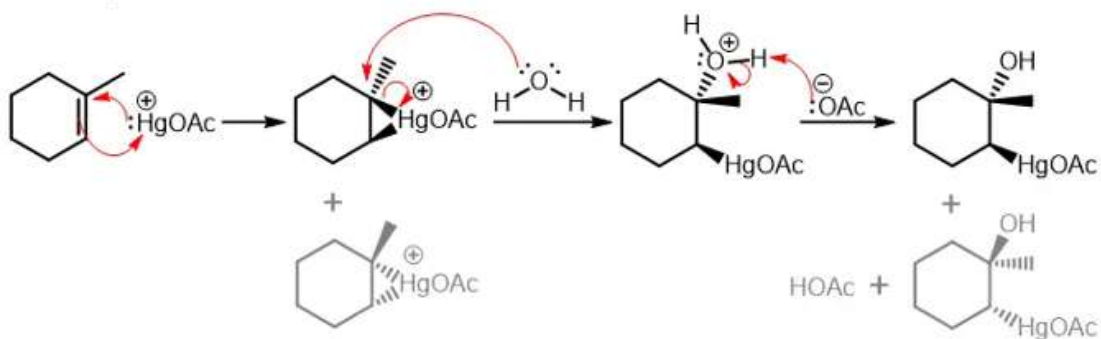
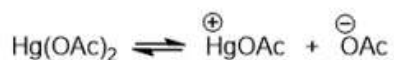
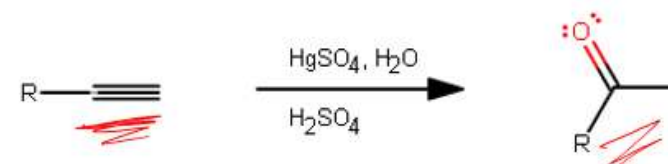
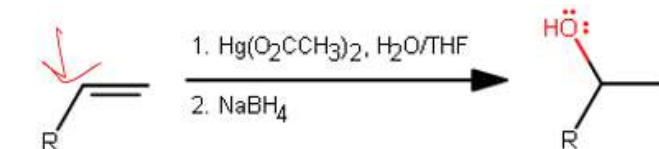
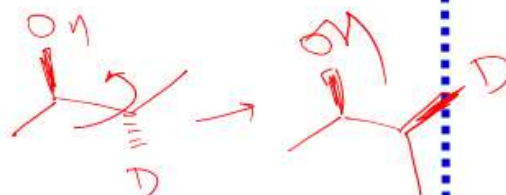
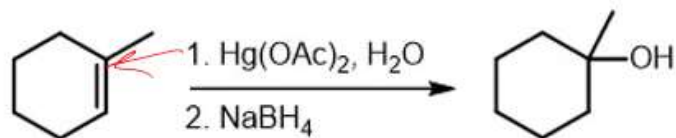




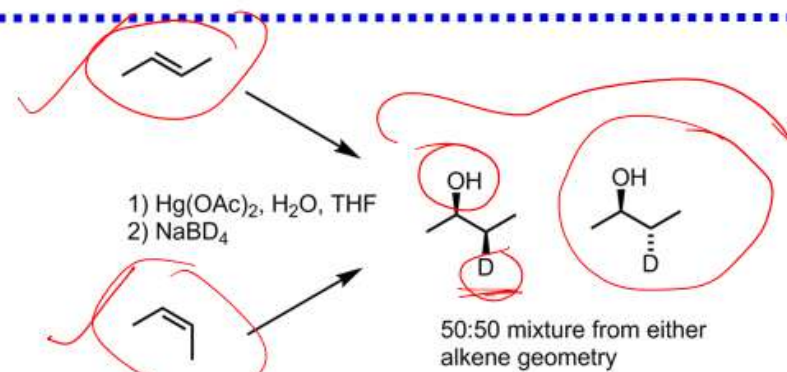


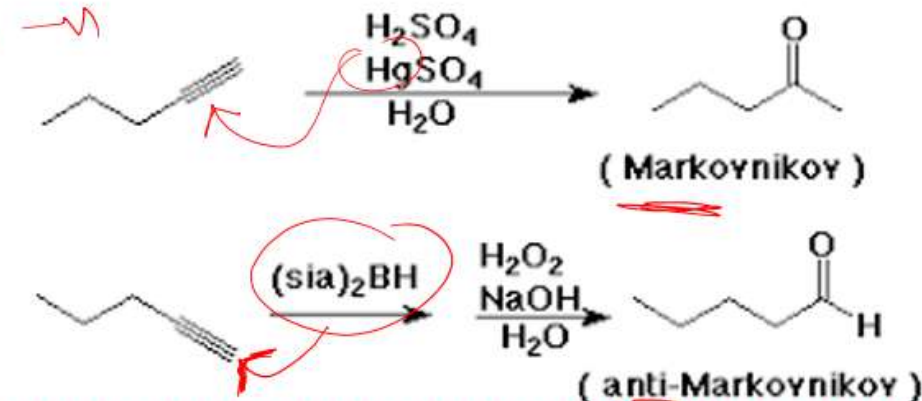
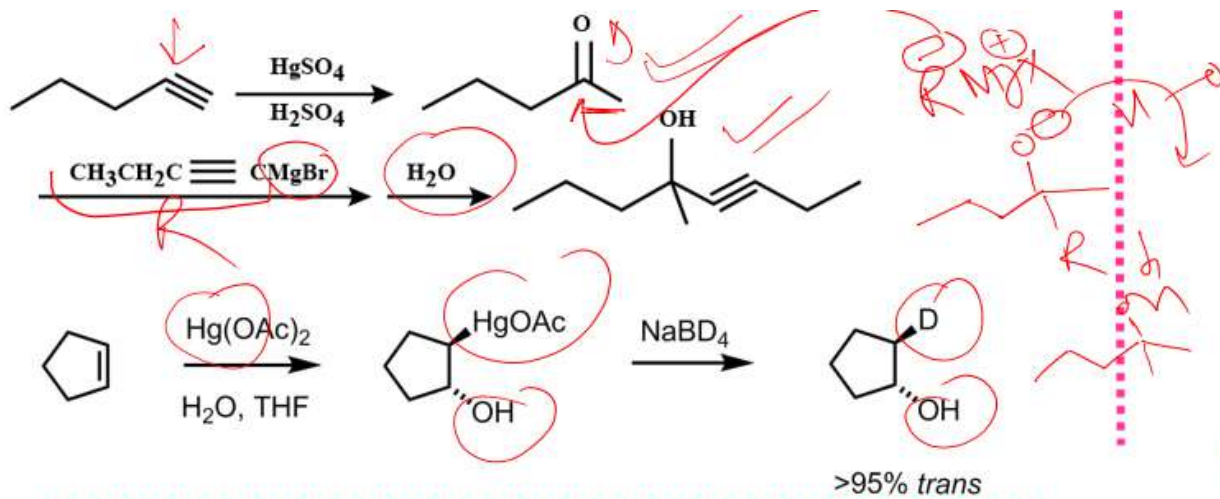
## Markovnikov addition of water - avoiding rearrangements



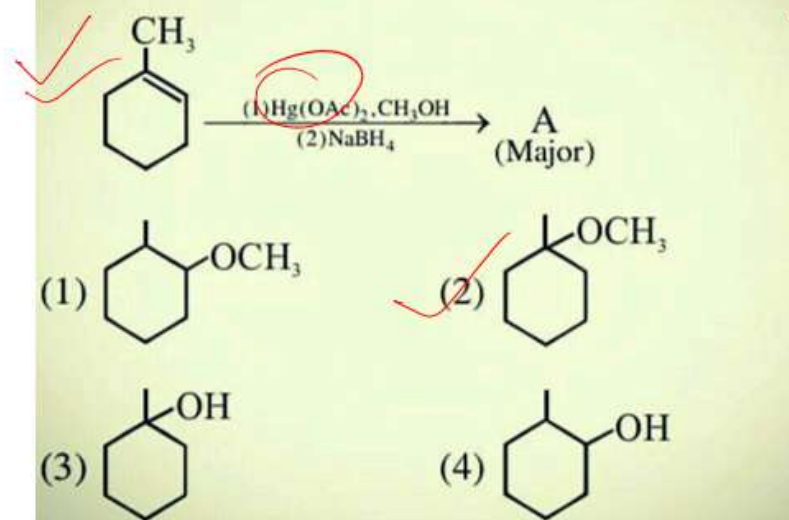


When *cis*- and *trans*-butene were subjected to the same process in independent experiments, in both cases the result was a 50:50 mixture of *syn*- and *anti*-stereochemistries. This indicates that there is cleavage of the carbon-mercury bond and sufficient lifetime for the resulting intermediate to undergo bond rotation before carbon-hydrogen bond formation. For other substrates, C-C bond rearrangements were observed.

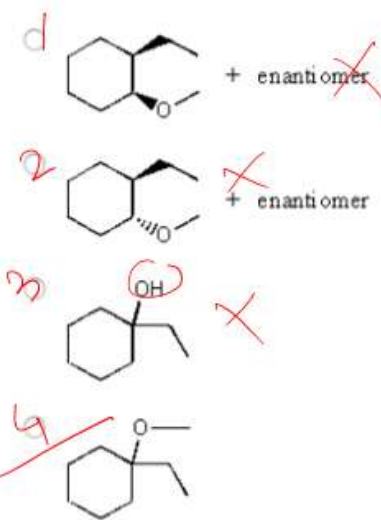
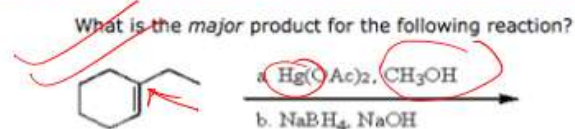
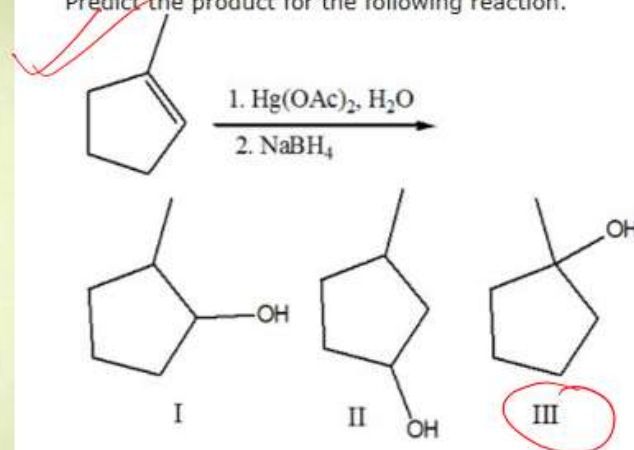




The product (A) of given oxymercuration demercuration is :-



Predict the product for the following reaction.



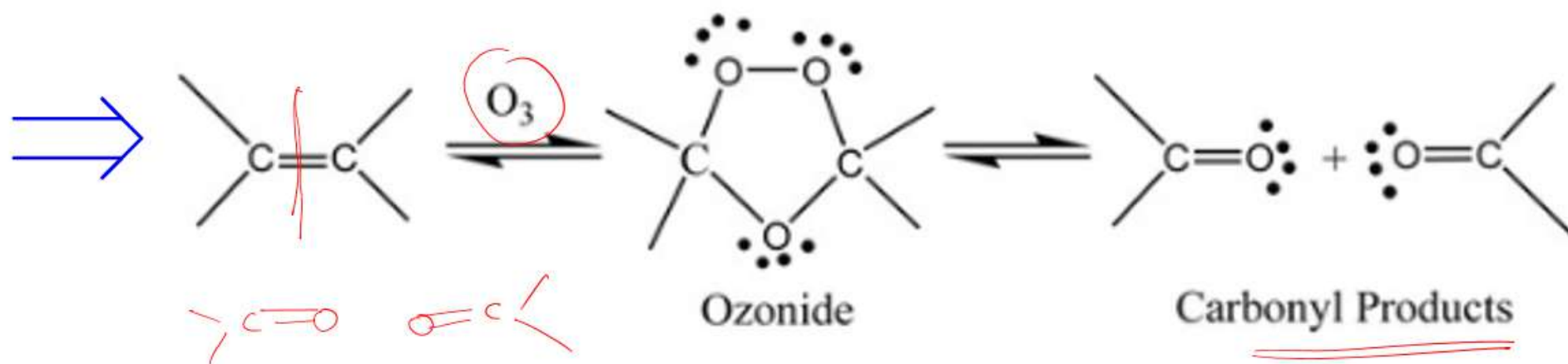
None of these choices.



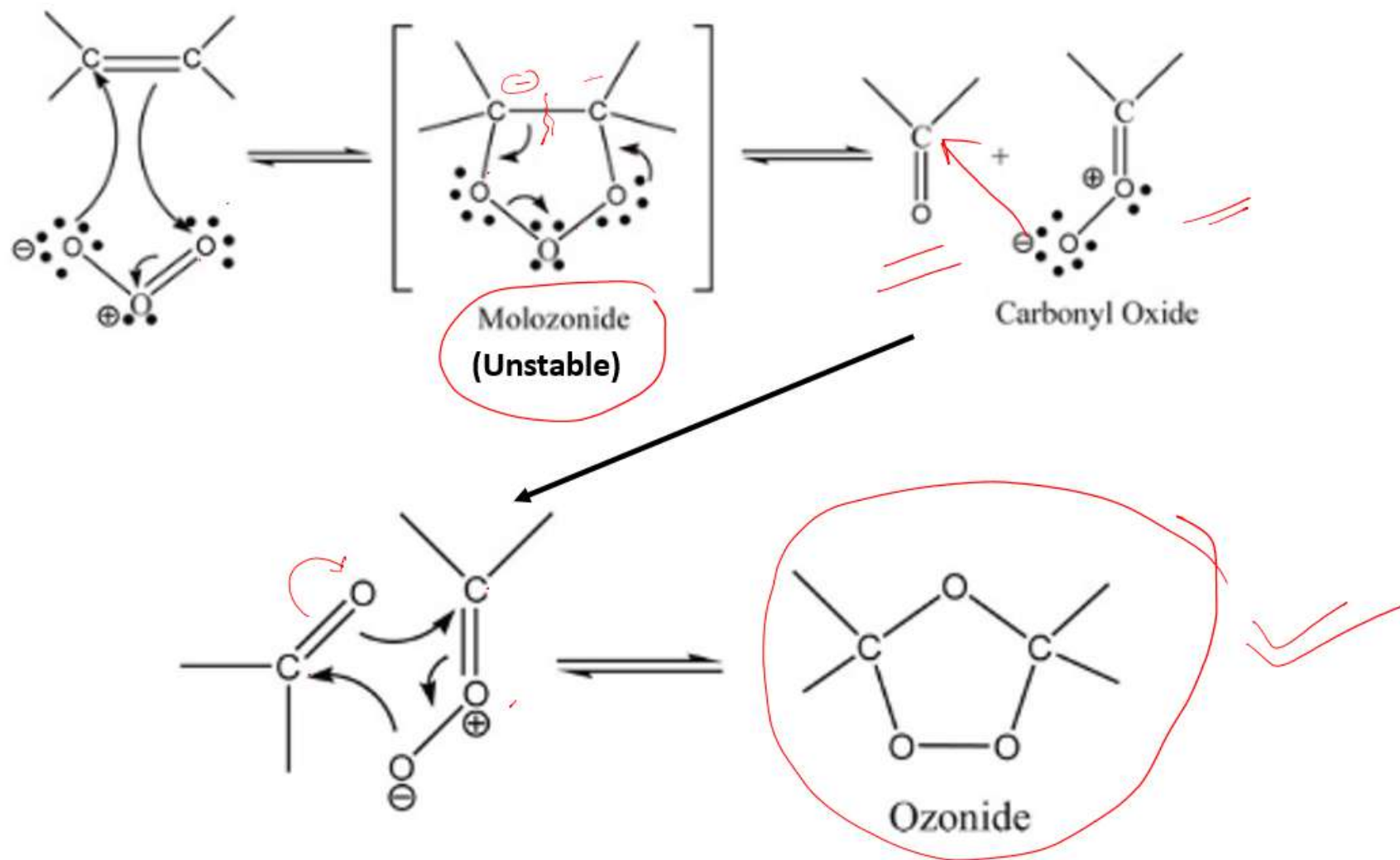
## Ozonolysis of alkene – Oxidation reaction

Ozonolysis is an organic reaction where the unsaturated bonds of alkenes, alkynes, or azo compounds are cleaved with ozone. Alkenes and alkynes form organic compounds in which the multiple carbon-carbon bond has been replaced by a carbonyl group while azo compounds form nitrosamines.

□ Ozone is an electrophilic reagent. Its structure is considered as a resonance hybrid of the following four canonical forms (each oxygen atom being  $sp^2$  hybridized).

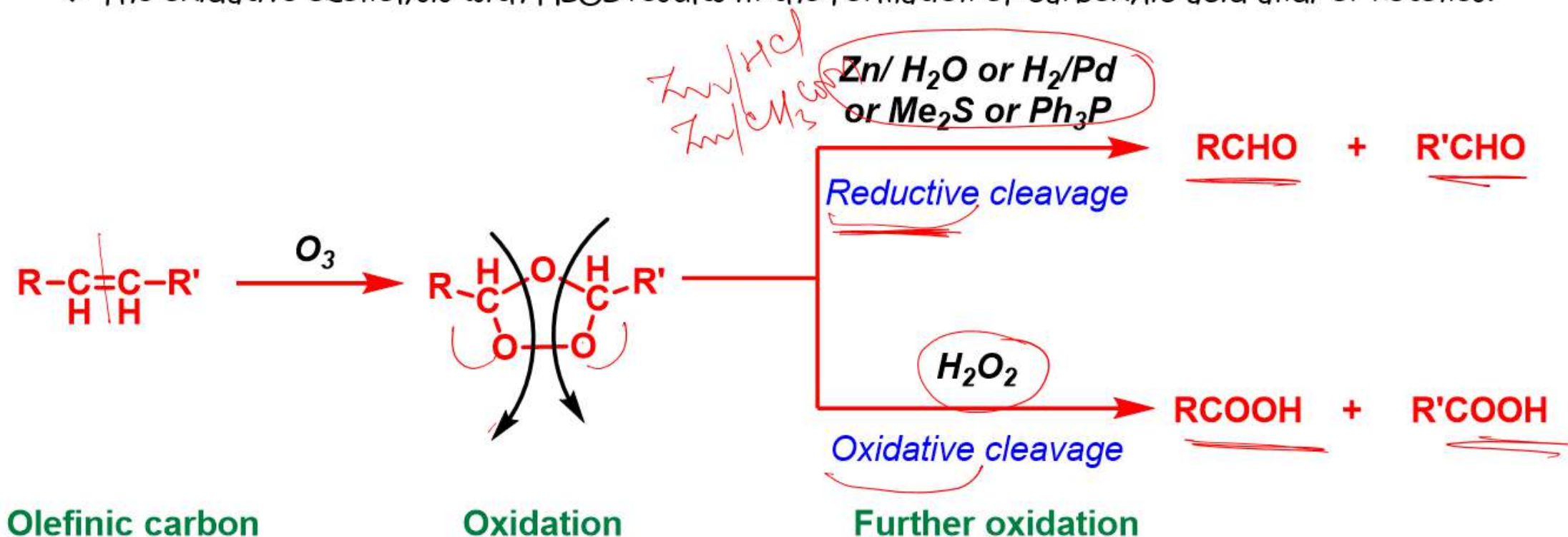


MECHANISM:



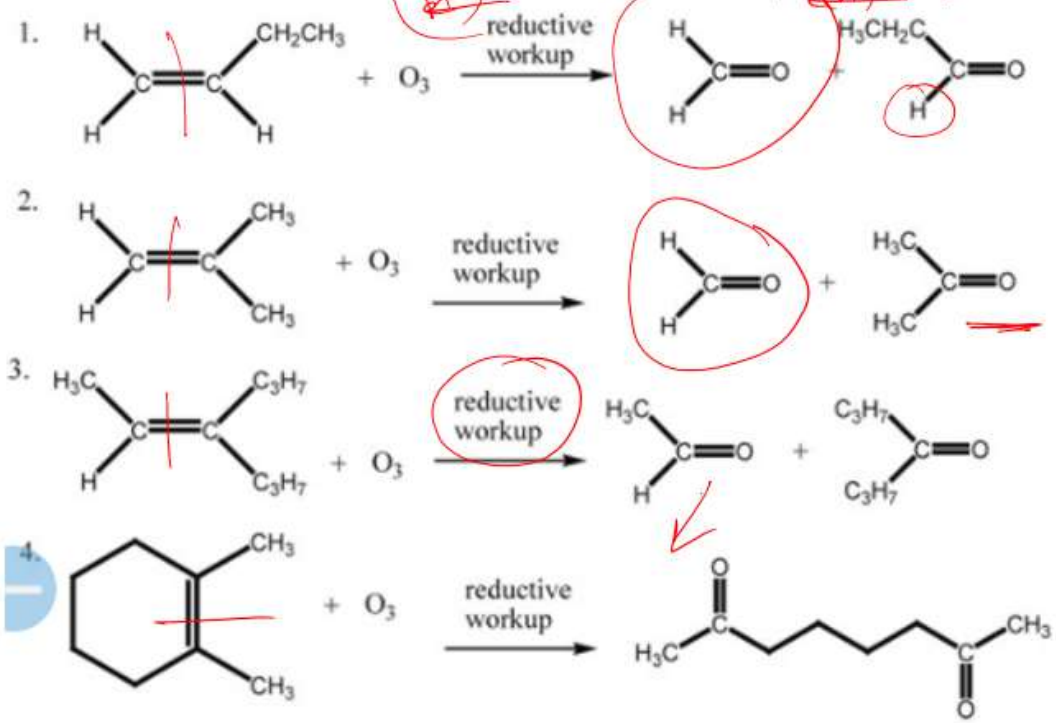
★ The ozonide being explosive in nature are not isolated as such. Further, the decomposition of ozonide is carried by reduction (known as reductive cleavage) or by oxidation (known as oxidative ozonolysis).

- ❖ The reductive ozonolysis with Zn, H<sub>2</sub>O results in the formation of aldehydes and/ or ketones.
- ❖ The oxidative ozonolysis with H<sub>2</sub>O<sub>2</sub> results in the formation of carboxylic acid and/ or ketones.

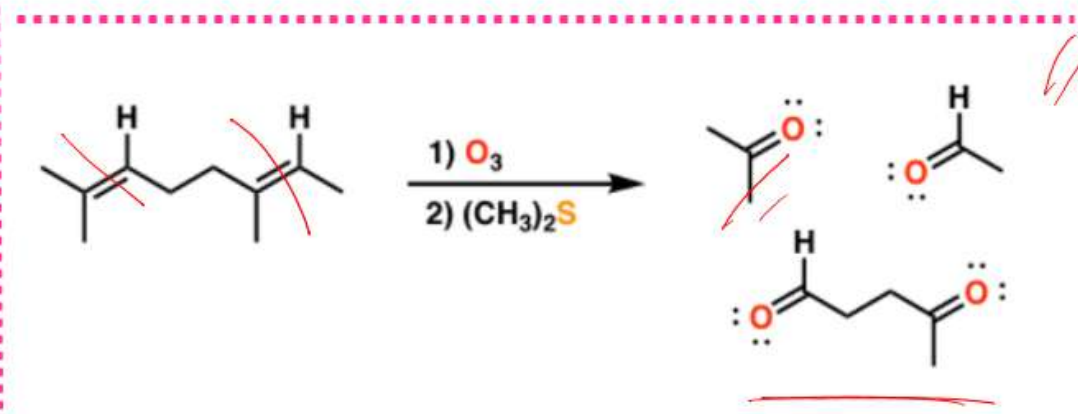
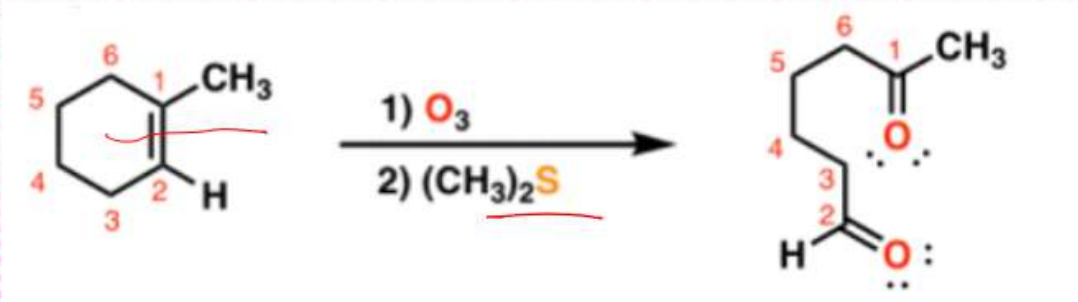
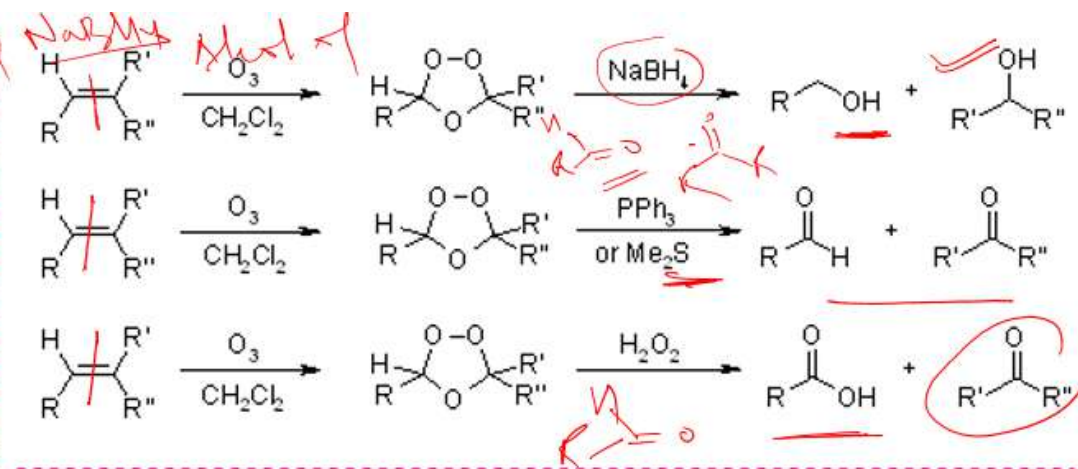
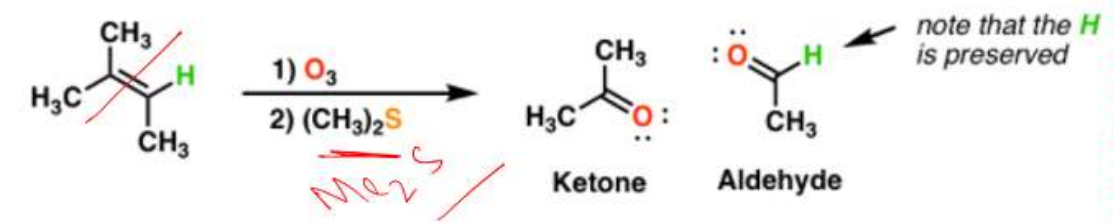




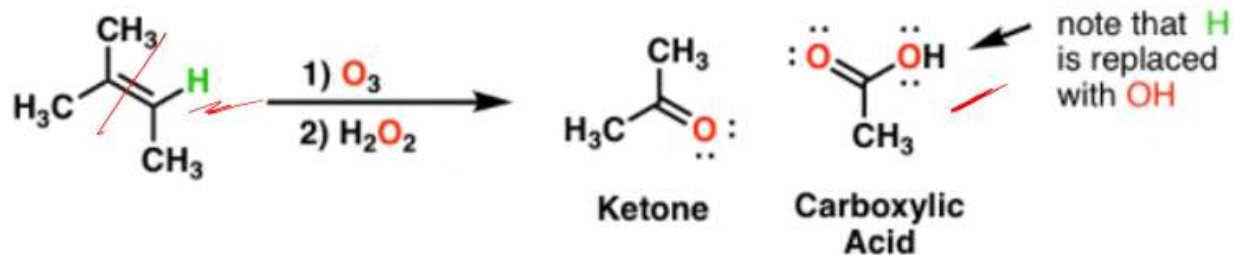
# EXAMPLES:



"Reductive workup" merely cleaves the C=C bond and replaces with oxygen



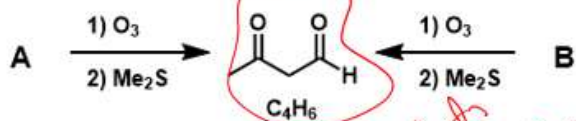
"Oxidative workup" oxidizes  $sp^2$  hybridized C-H bonds to C-OH as well as cleaving C=C



Typical oxidant used for "oxidative workup" is  $\text{H}_2\text{O}_2$ ; this oxidizes any aldehydes to carboxylic acids

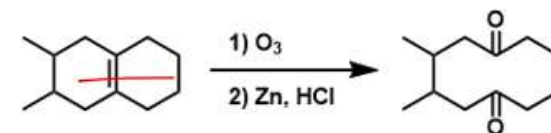
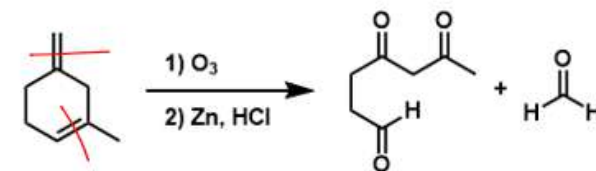
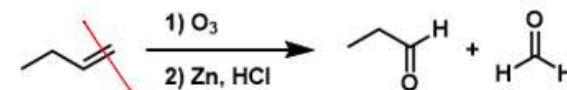
The same process can be performed by replacing  $\text{O}_3$  with hot, acidic  $\text{KMnO}_4$

Two constitutional isomers of the compound  $\text{C}_8\text{H}_{12}$ , A and B, both yield a single product following ozonolysis. Determine the structures of A and B.

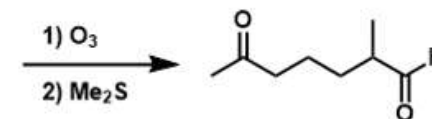
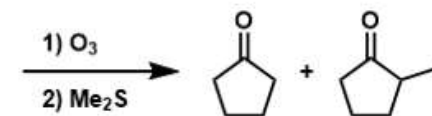
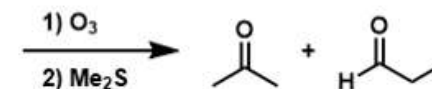


*Reacts re change*

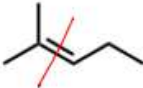

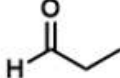
Draw the products of the following ozonolysis reactions.



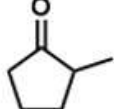


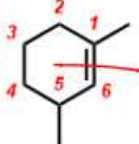

Draw the reactant for the following ozonolysis reactions.

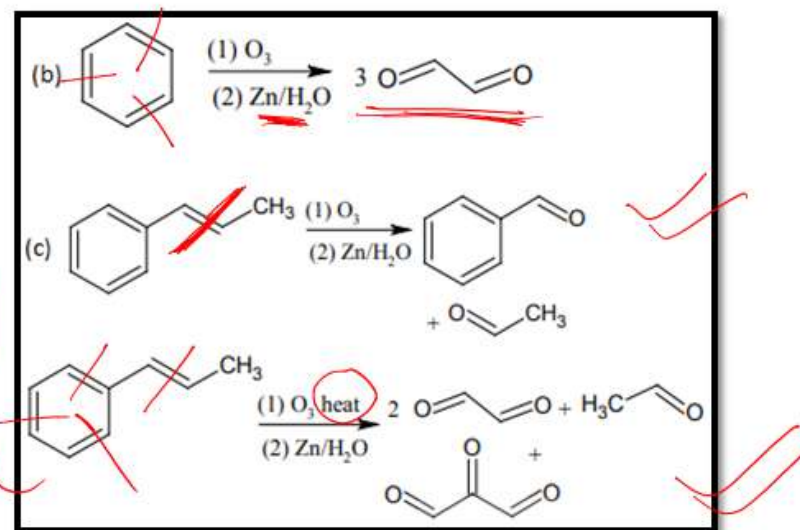
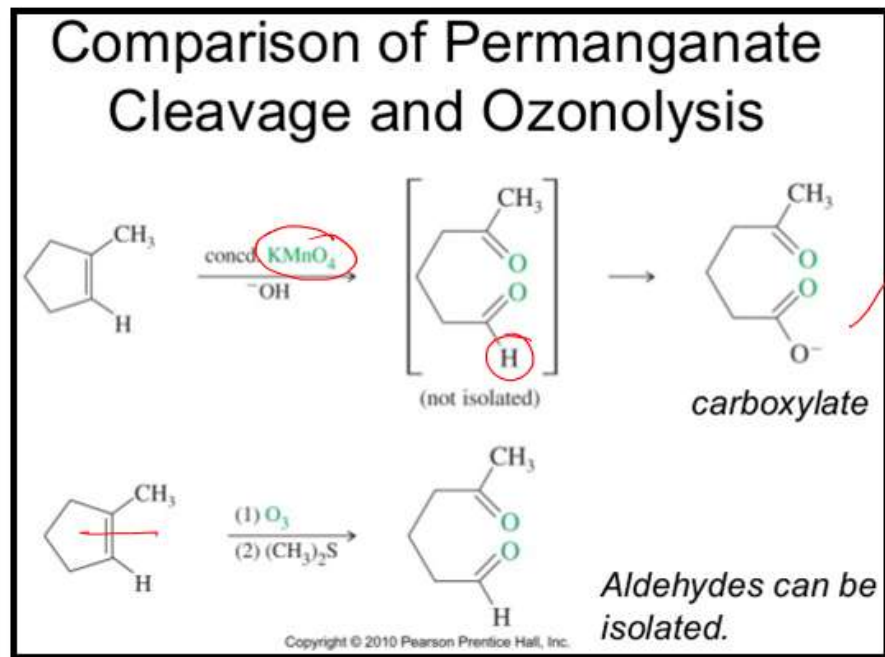


Draw the reactant for the following ozonolysis reactions.

Reaction 1:   $\xrightarrow[2) \text{Me}_2\text{S}]{1) \text{O}_3}$   + 

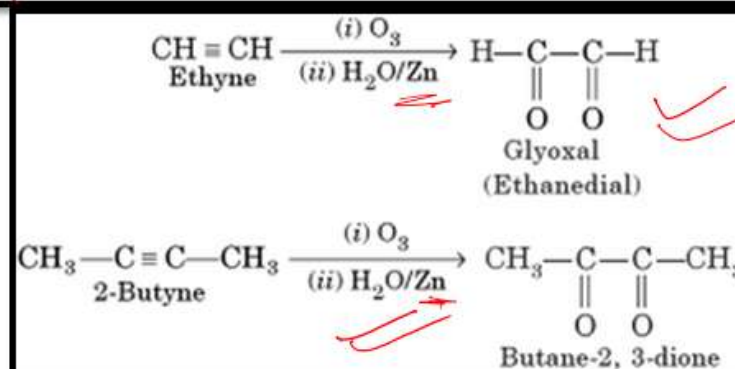
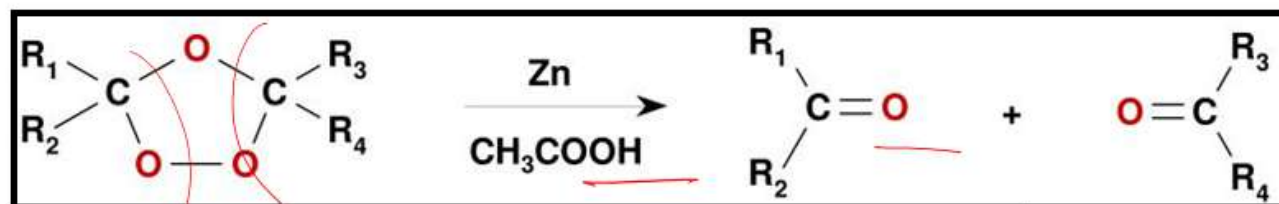
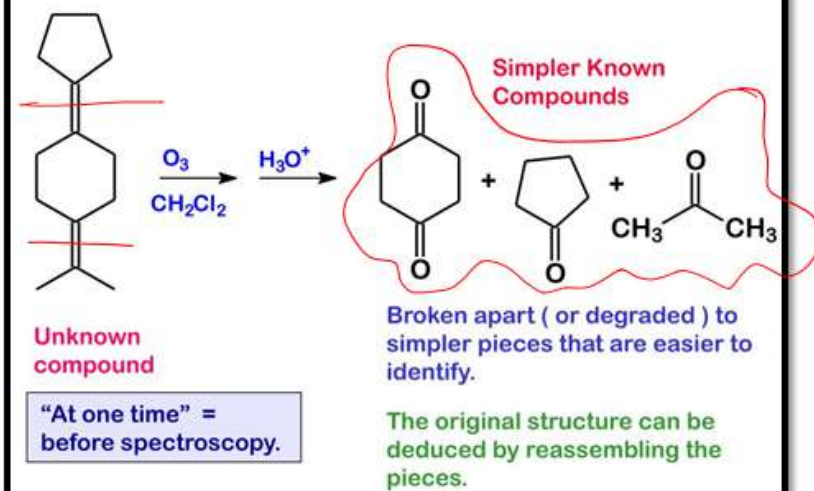
Reaction 2:   $\xrightarrow[2) \text{Me}_2\text{S}]{1) \text{O}_3}$   + 

Reaction 3:   $\xrightarrow[2) \text{Me}_2\text{S}]{1) \text{O}_3}$  

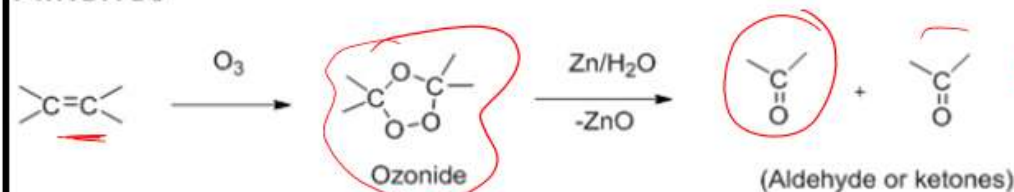




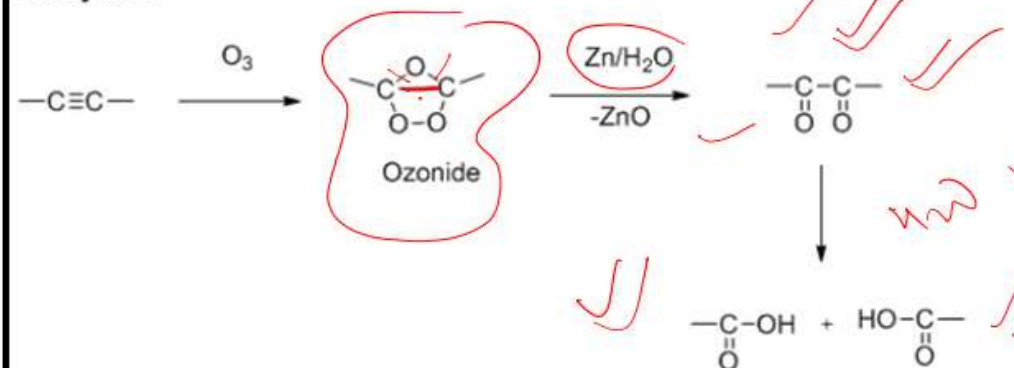
**AT ONE TIME OZONOLYSIS WAS WIDELY USED FOR STRUCTURE PROOF BY DEGRADATION**



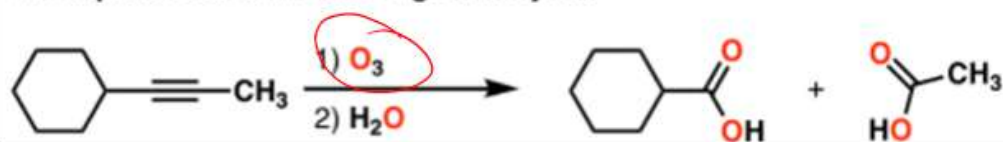
**Alkenes**

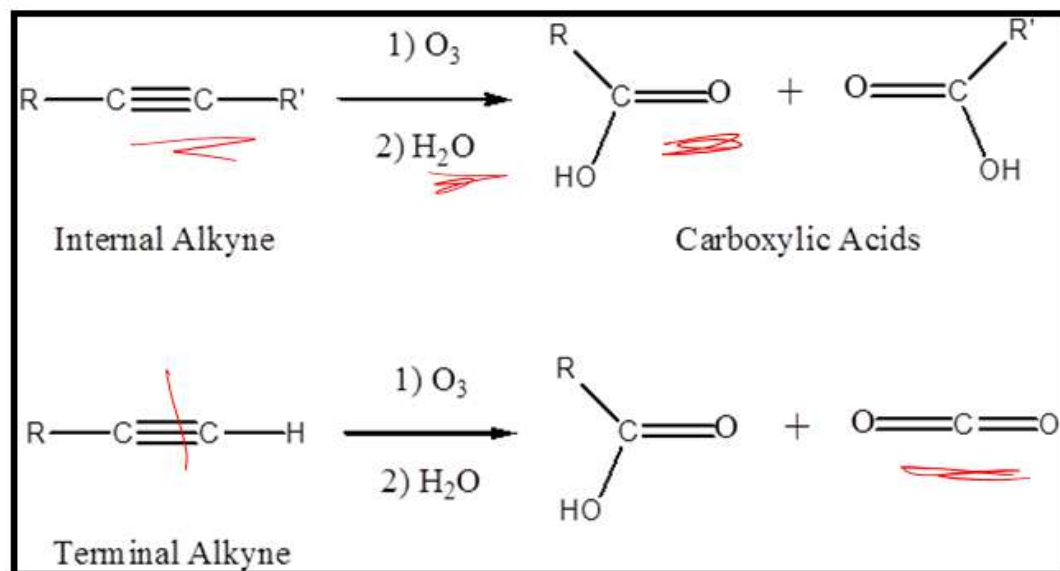
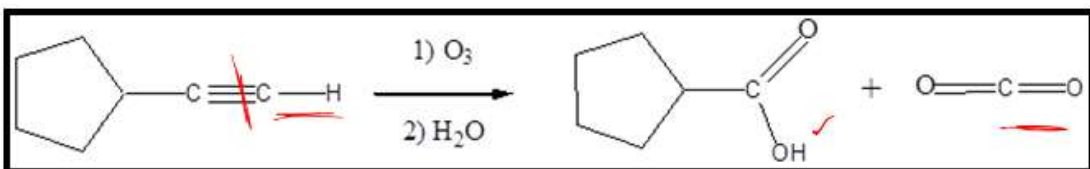
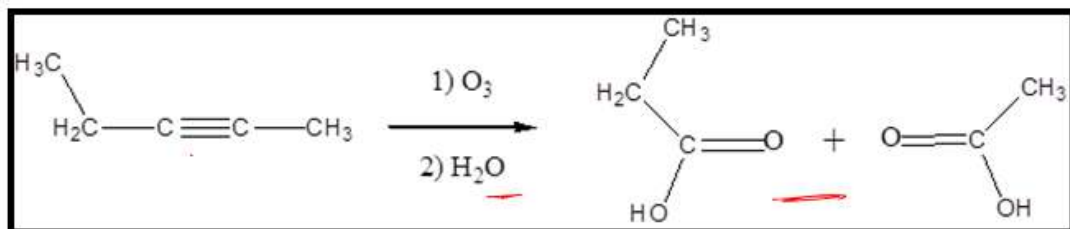
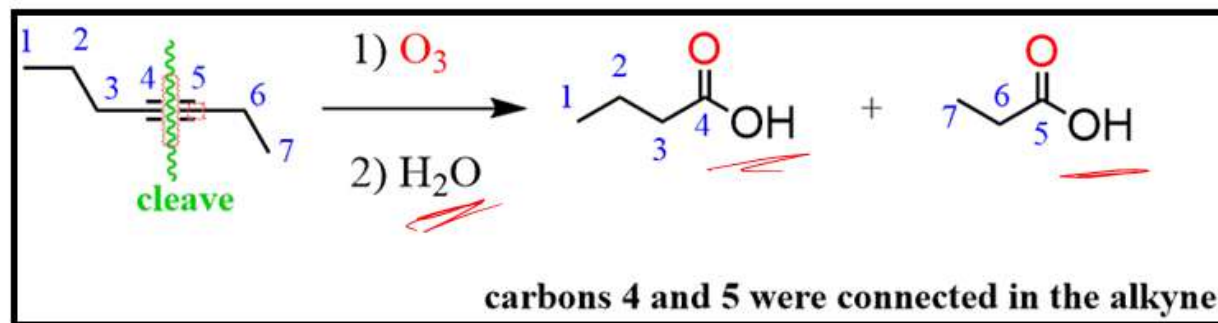
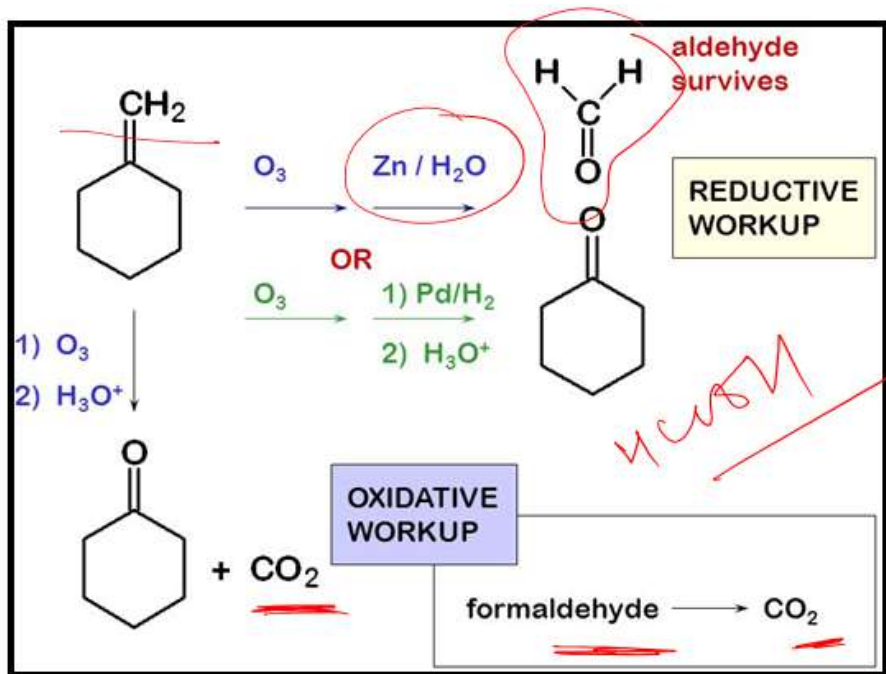


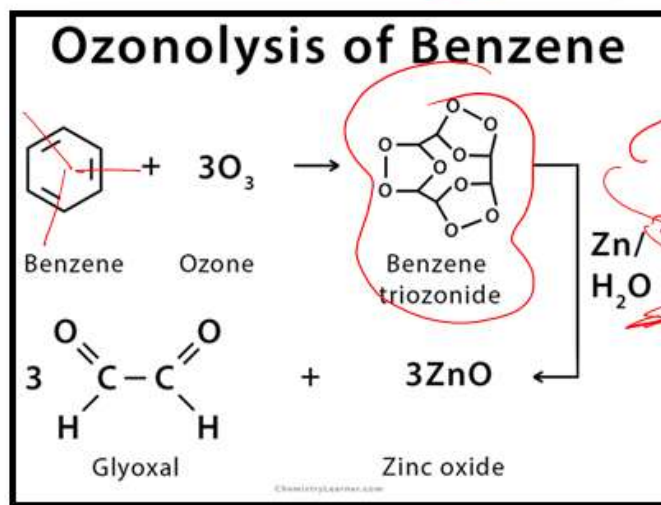
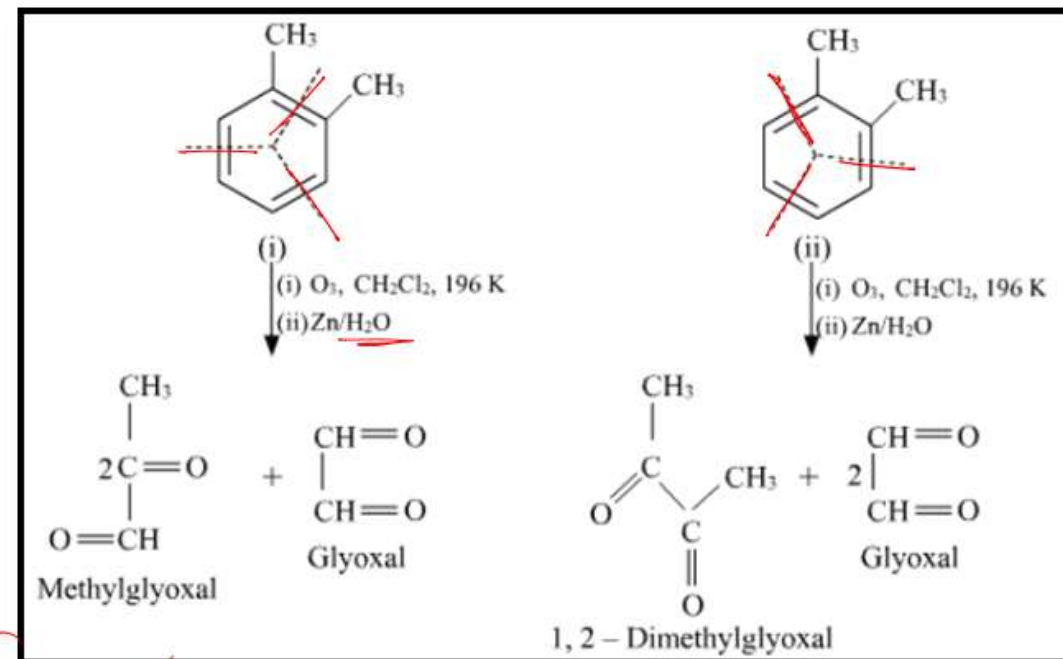
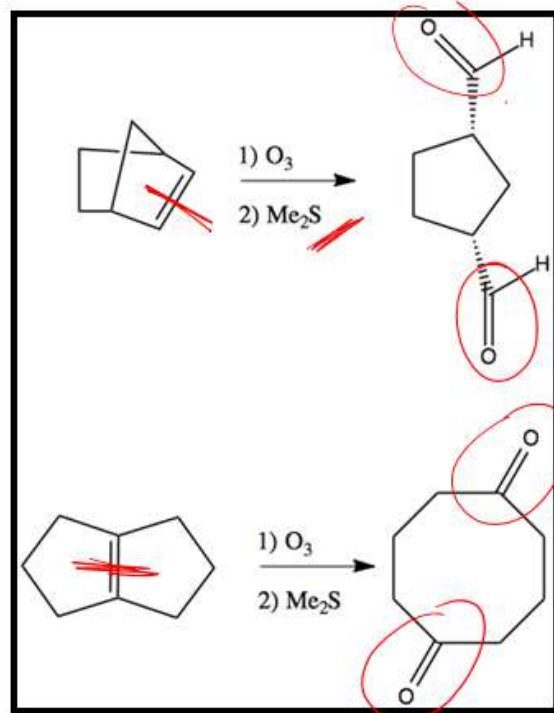
**Alkynes**



**Example 3: Oxidative cleavage of alkynes**







*Handwritten notes:*  
 1) Methylglyoxal  
 2) Methylglyoxal  
 3) Methylglyoxal  
 4) Methylglyoxal  
 5) Methylglyoxal  
 6) Methylglyoxal  
 7) Methylglyoxal  
 8) Methylglyoxal  
 9) Methylglyoxal  
 10) Methylglyoxal

