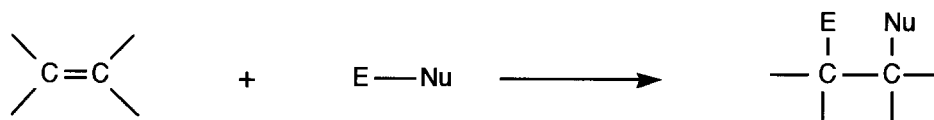


Chapter 8: Reactions of Alkenes (omit 8-5a and 8-16)

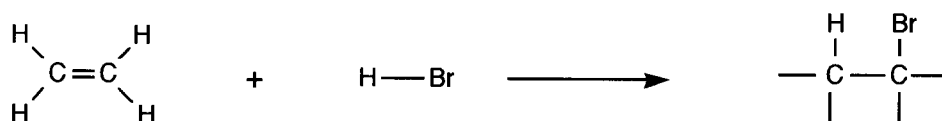
Electrophilic Additions: (addition of E⁺)

NOTICE: THIS MATERIAL MAY BE PROTECTED BY
COPYRIGHT LAW "TITLE 17 U.S. CODE"

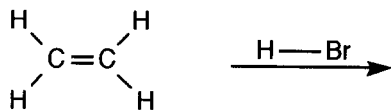
General:



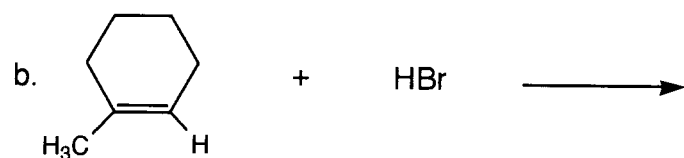
I. Addition of HX (HCl, HBr, HI)



Mechanism:



Addition to unsymmetrical alkenes:

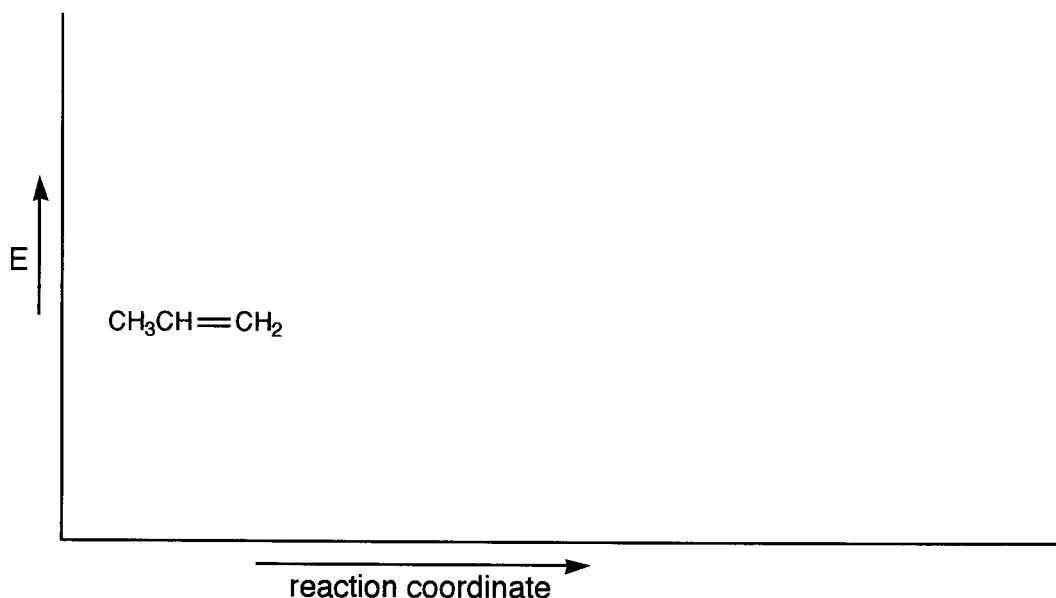


Regiospecific: product is formed from only one of two possible orientations of addition

Markovnikov's Rule (observation): The addition of HX to the double bond of an alkene results in a product with the acidic proton bonded to the carbon that already has the greater number of hydrogens.

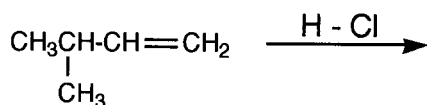
WHY?

What is RDS?

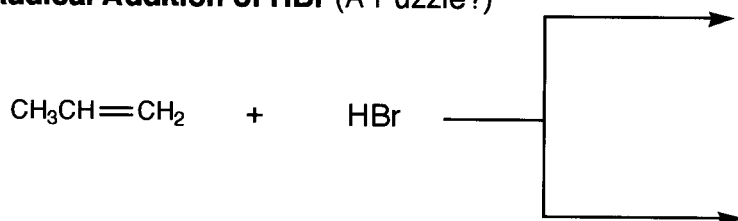


Mark's Rule (extended): In an electrophilic addition, E^+ adds in a way that generates the most stable intermediate.

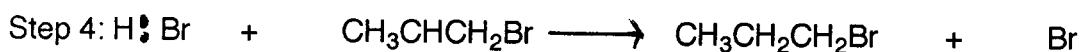
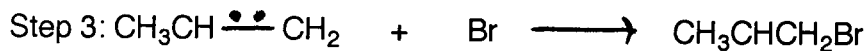
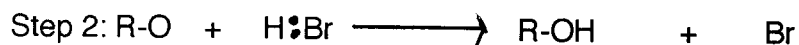
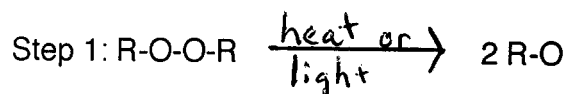
Example:



Free Radical Addition of HBr (A Puzzle?)



Peroxide Effect: (Only with HBr)

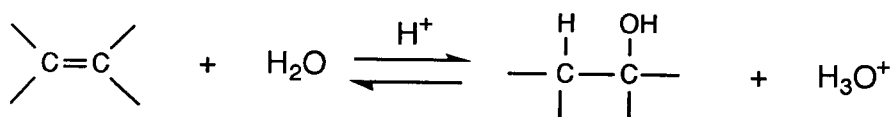


without peroxide:

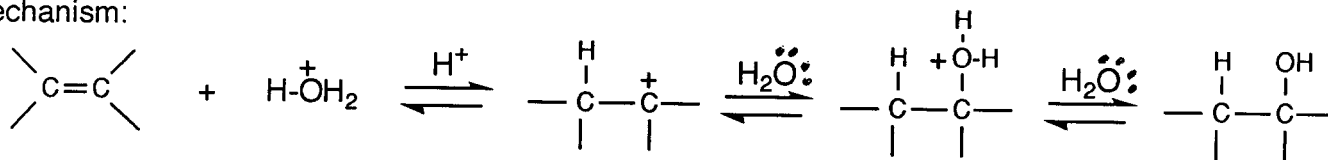
with peroxide:

II. Addition of H-OH:

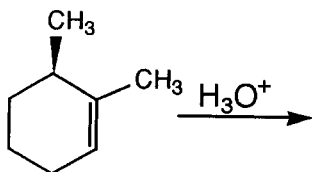
A. Hydration - acid catalyzed addition of H₂O across double bond
- reverse of dehydration of alcohols



Mechanism:

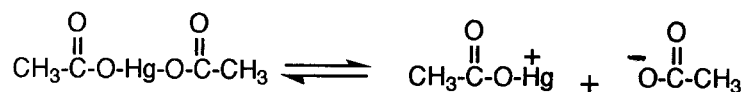
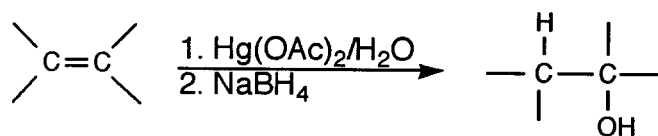


Example:

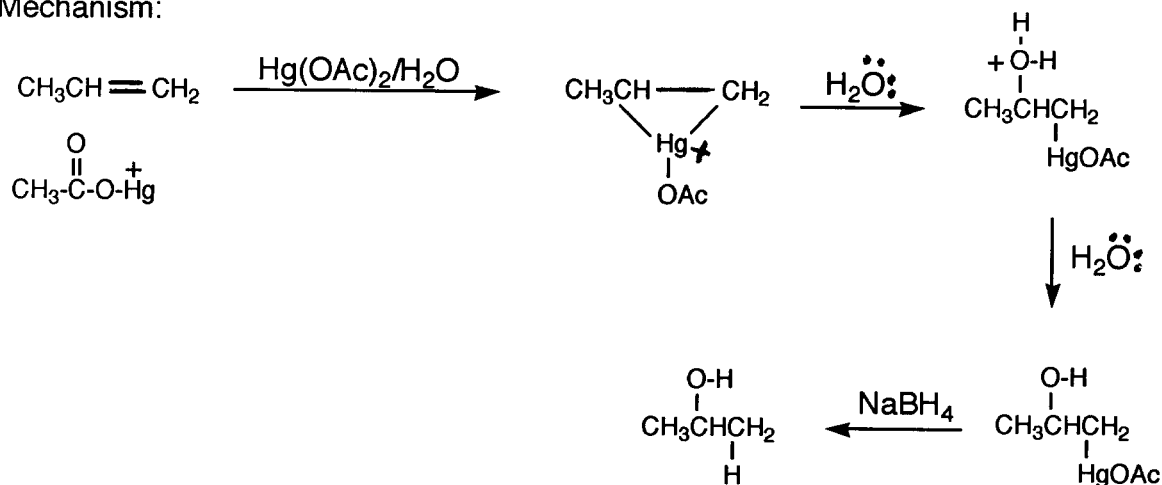


B. Indirect hydration - product is alcohol, but not from direct addition of H₂O

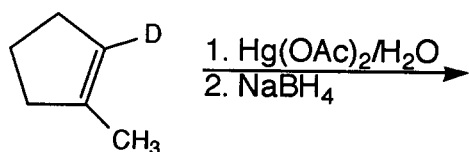
1. Oxymercuration/demercuration



Mechanism:

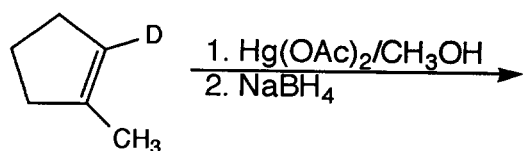


Example:

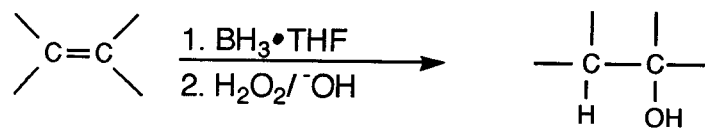


useful variation: alkoxymercuration/demercuration - use an alcohol instead of H₂O to form ethers
mechanism, stereochemistry, and regiochemistry same as above

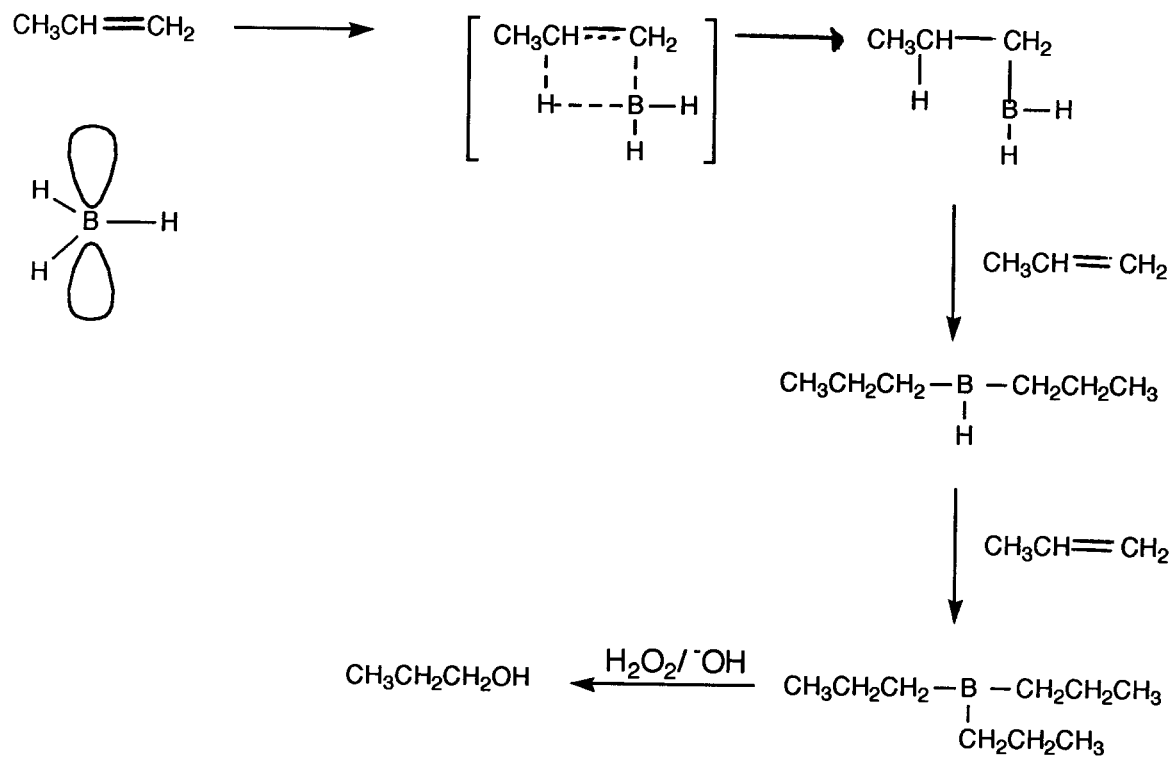
Example:



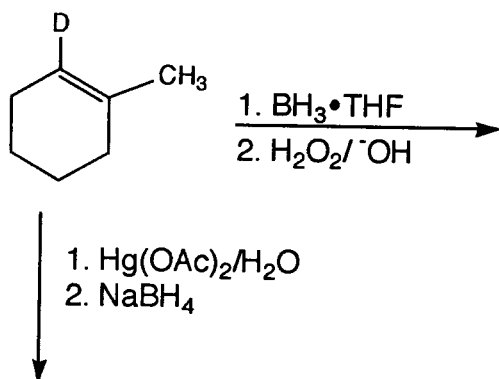
2. Hydroboration



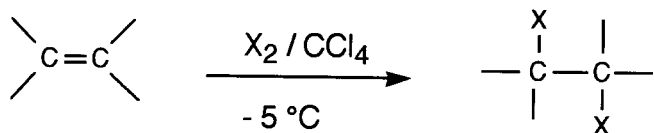
Mechanism:



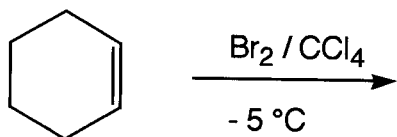
Examples:



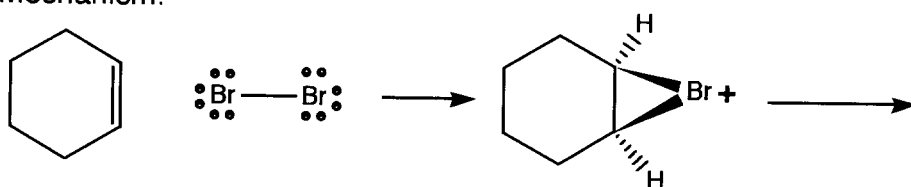
IV. Addition of X-X (halogens: Cl₂, Br₂, sometimes I₂)



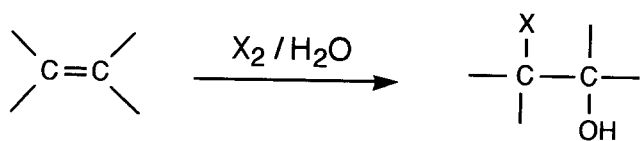
Example:



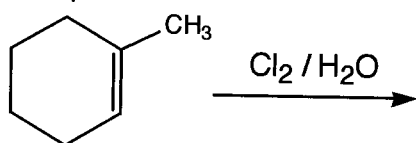
Mechanism:



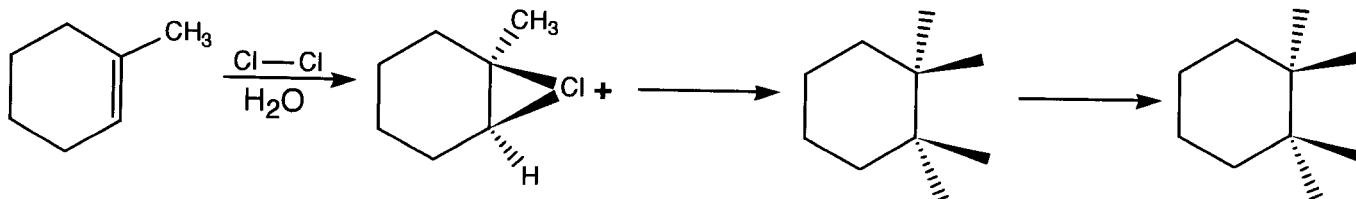
V. Addition of X-OH (from X₂ / H₂O): Halohydrin Formation



Example:

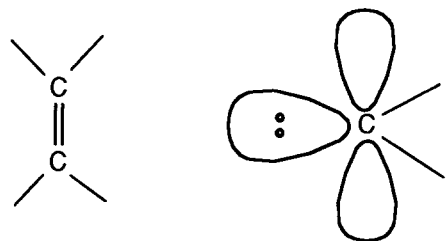


Mechanism:

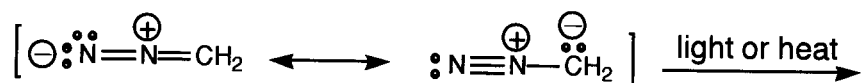


VI. Addition of Carbenes and Carbenoid Species

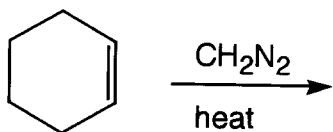
General:



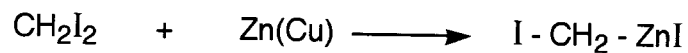
A. Methylene: :CH_2 from diazomethane (CH_2N_2)



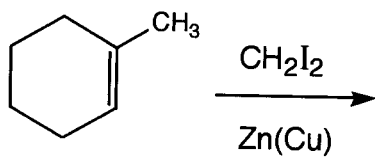
Example:



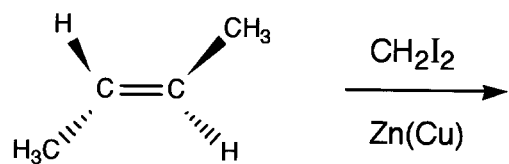
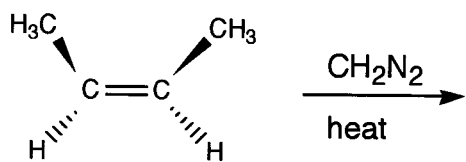
B. Simmons-Smith Reagent (produces carbenoid species)



Example:

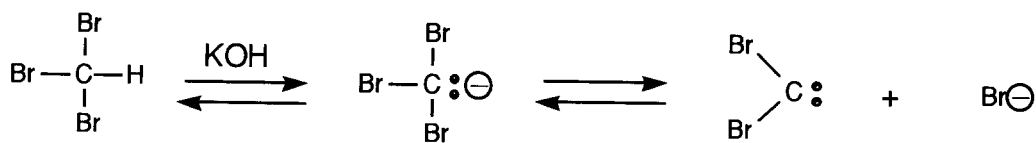
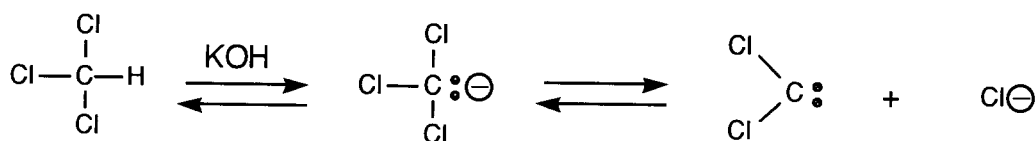


NOTE: The stereochemistry of the alkene is always maintained in carbene/carbenoid additions.

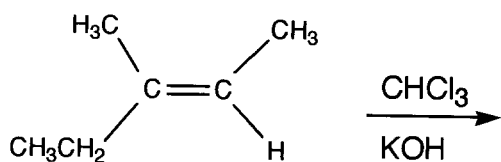


C. Dibromocarbene and Dichlorocarbene

Formation of carbene:



Example:

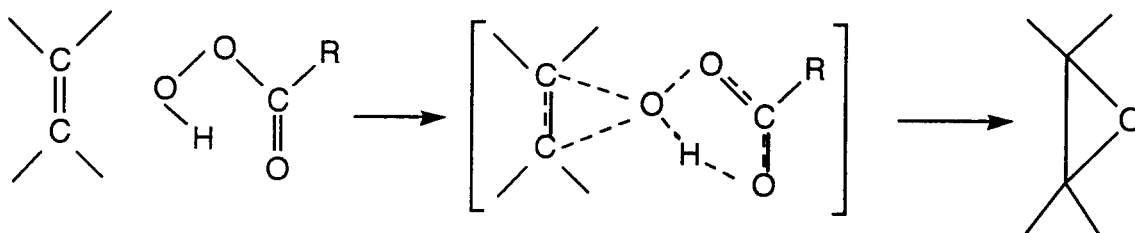


Oxidation of Alkenes

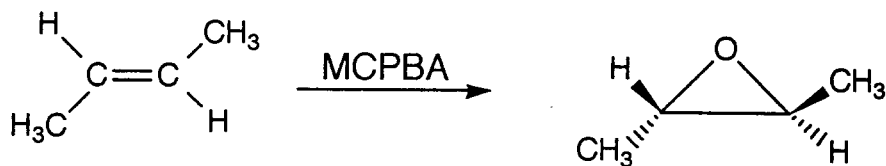
A. Epoxidation with peroxyacids:



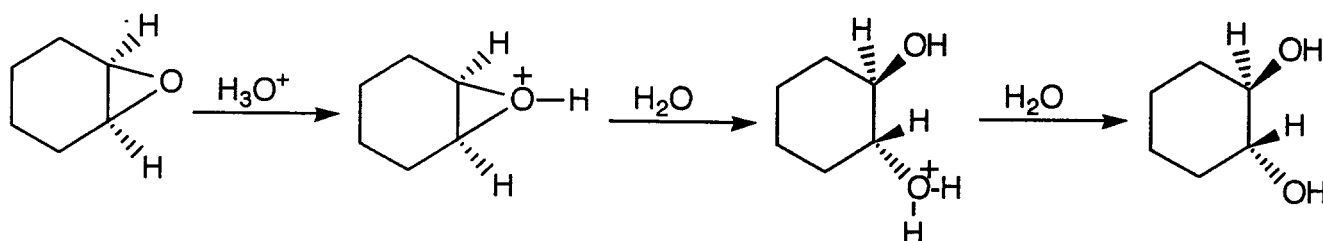
Mech: a concerted process



Stereochemistry of the alkene is maintained:



Acid - catalyzed ring opening of epoxides:

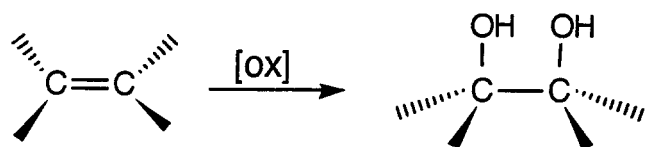


Isolation of epoxide vs diol:

* Strongly acidic peroxyacids in aqueous solution give diol (epoxide not isolated).

* Weakly acidic peroxyacids in nonaqueous solution give epoxide.

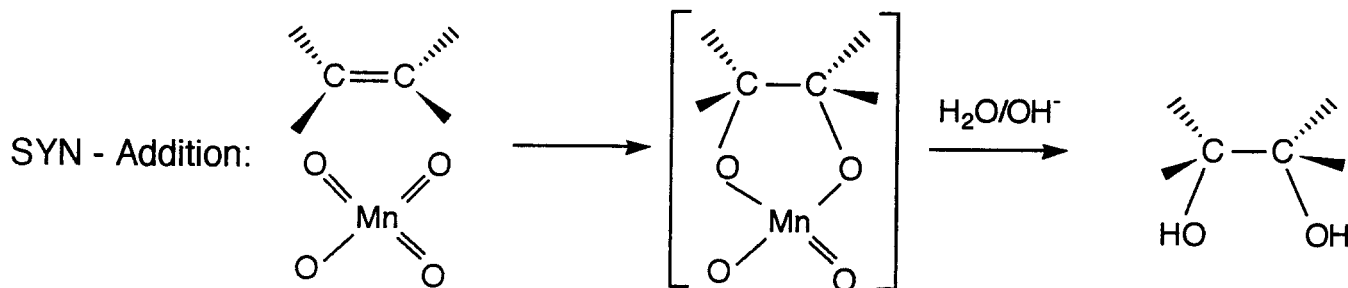
B. Hydroxylation



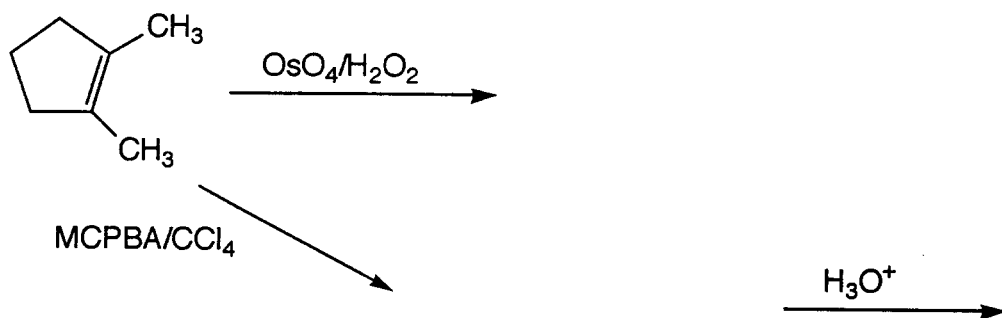
[ox] :

1. COLD, basic KMnO_4

2. $\text{OsO}_4 / \text{H}_2\text{O}_2$



Example:



C. Oxidative Cleavage

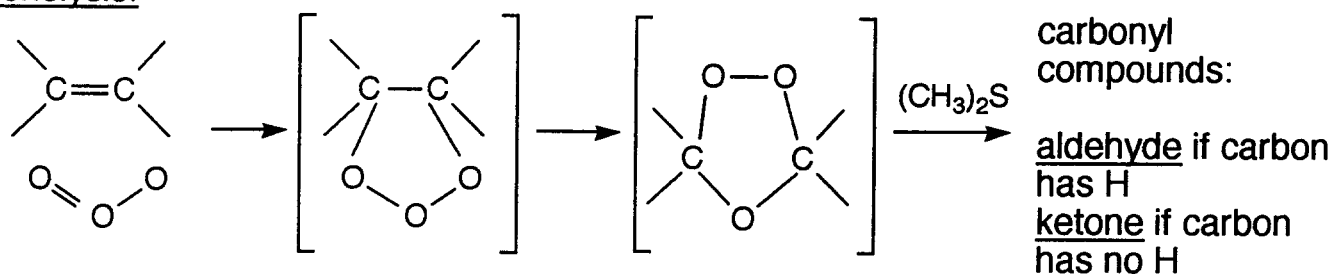


[ox] :

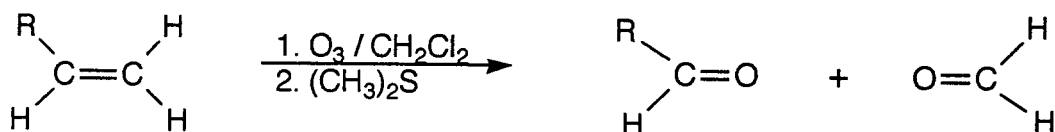
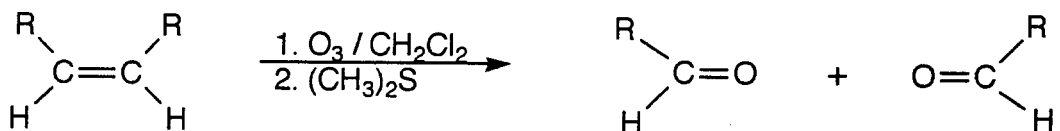
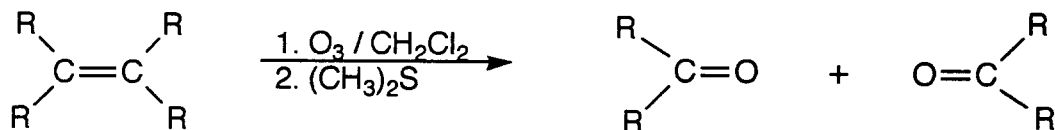
1. WARM, concentrated KMnO_4 , acidic or neutral conditions

2. Ozonolysis: 1) O_3 2) $(\text{CH}_3)_2\text{S}$ or $\text{Zn}/\text{acetic acid}$

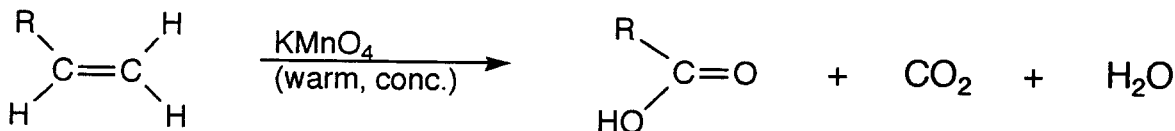
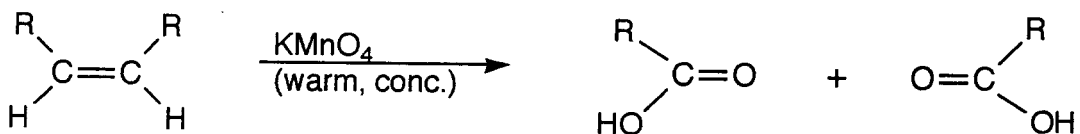
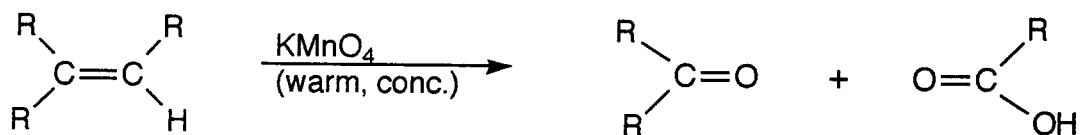
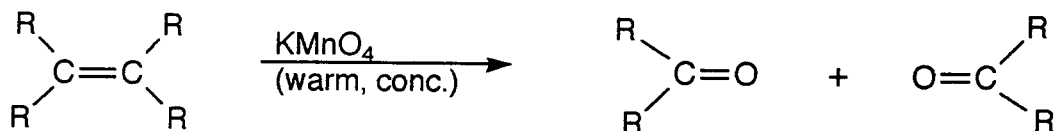
Ozonolysis:



General examples:



Warm KMnO_4 cleavage: gives ketone if carbon has no H, gives carboxylic acid if carbon has H (KMnO_4 oxidizes aldehydes to carboxylic acids and formaldehyde to $\text{CO}_2 + \text{H}_2\text{O}$.)



Alkene Reaction Summary

