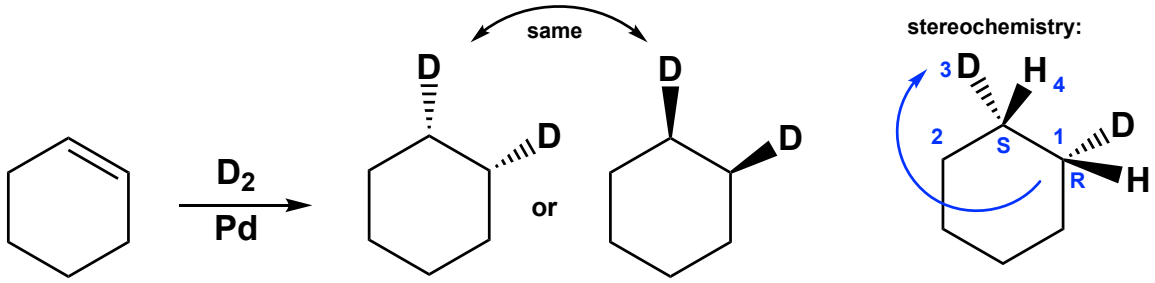
Review: Hydrogenation

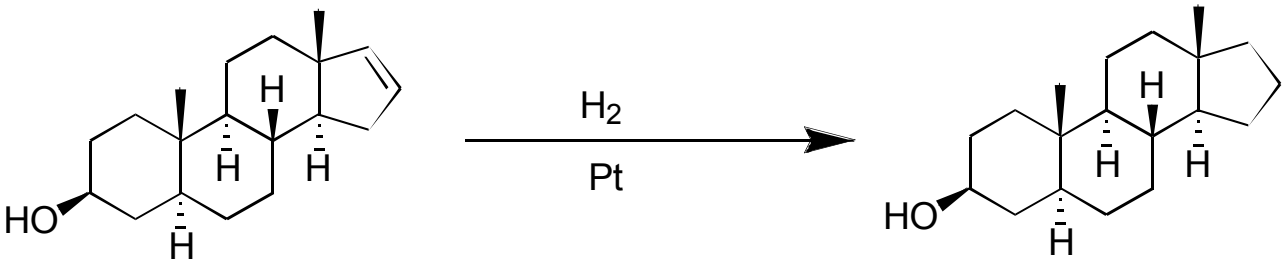
The addition of H_2 to an alkene

Example: cyclohexene

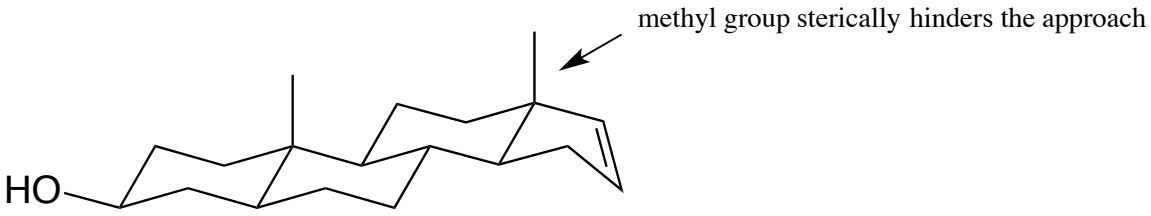


Aside: D = deuterium = ^2H ($1\ p^+$ and $1\ e^-$) Product is a **meso** compound (has stereogenic centers but is achiral due to plane of symmetry within molecule

*Example***:** androstane (steroid, male hormone)

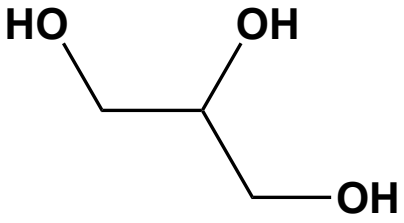


H_2 comes from the bottom only because the methyl group adjacent to the alkene shields the top face

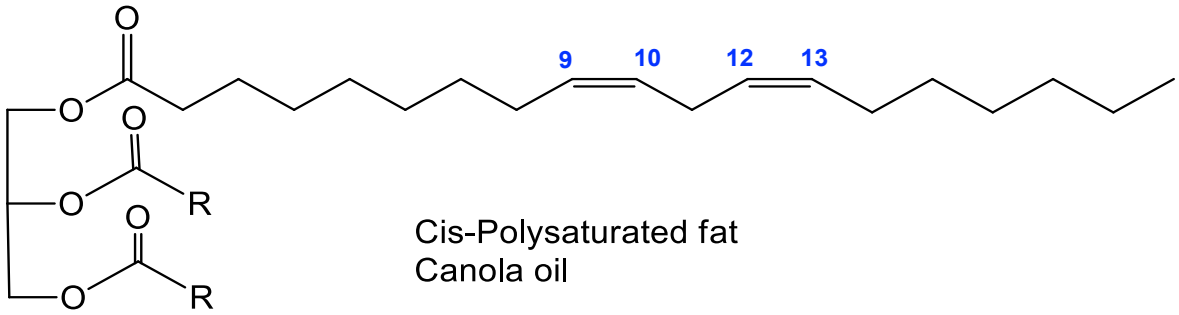


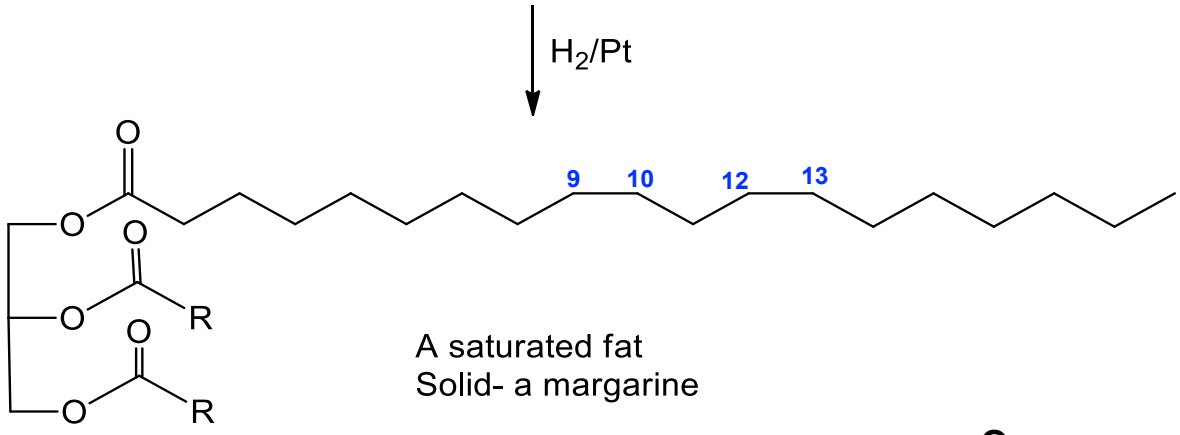
***Example*: fats** (esters of glycerol)

glycerol or glycerin:

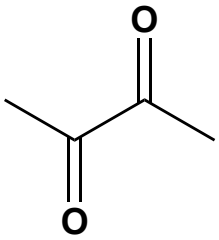


triglyceride: ester molecule composed of glycerol and three fatty acids





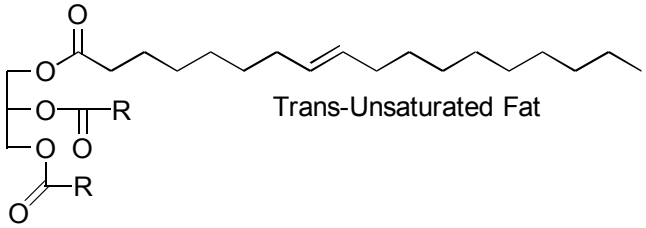
Aside: the colour of margarine is artificial, a yellow dye – Pearl (maragon) is added, hence the name 'margarine'
Additionally, diacetyl (on the right) is added and this gives it the familiar "buttery flavour"



Terminology

Unsaturated fat = double bond in the fatty acid, induces "kinks" in the carbon chain
Saturated fat = single bonds in the carbon chain (not including glycerol moiety)

Trans-unsaturated fat:

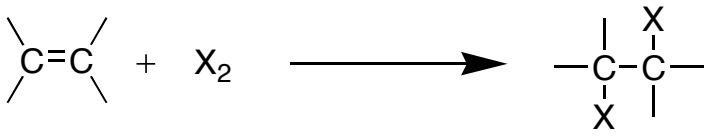


Trans-polyunsaturated fat = multiple double bonds, all with *trans* configuration
Cis-polyunsaturated fat = multiple double bonds, all with *cis* configuration

Halogenation

- The addition of a halide (X_2) to an alkene
- Reaction is fast and does not require heat or light as with alkane
- Addition occurs in anti or trans fashion
- Heterolytic chemistry (movement of 2 electrons)

General reaction

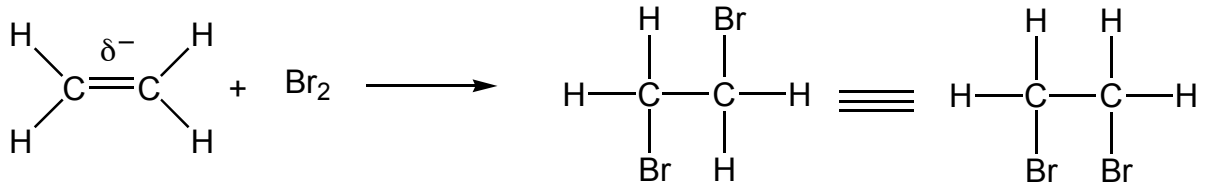


X= Cl or Br

Anti or trans addition

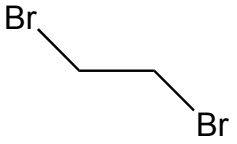
Examples:

Alkene

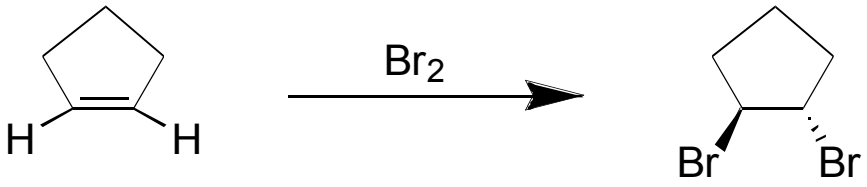


Anti or trans addition

Free rotation about C-C bond

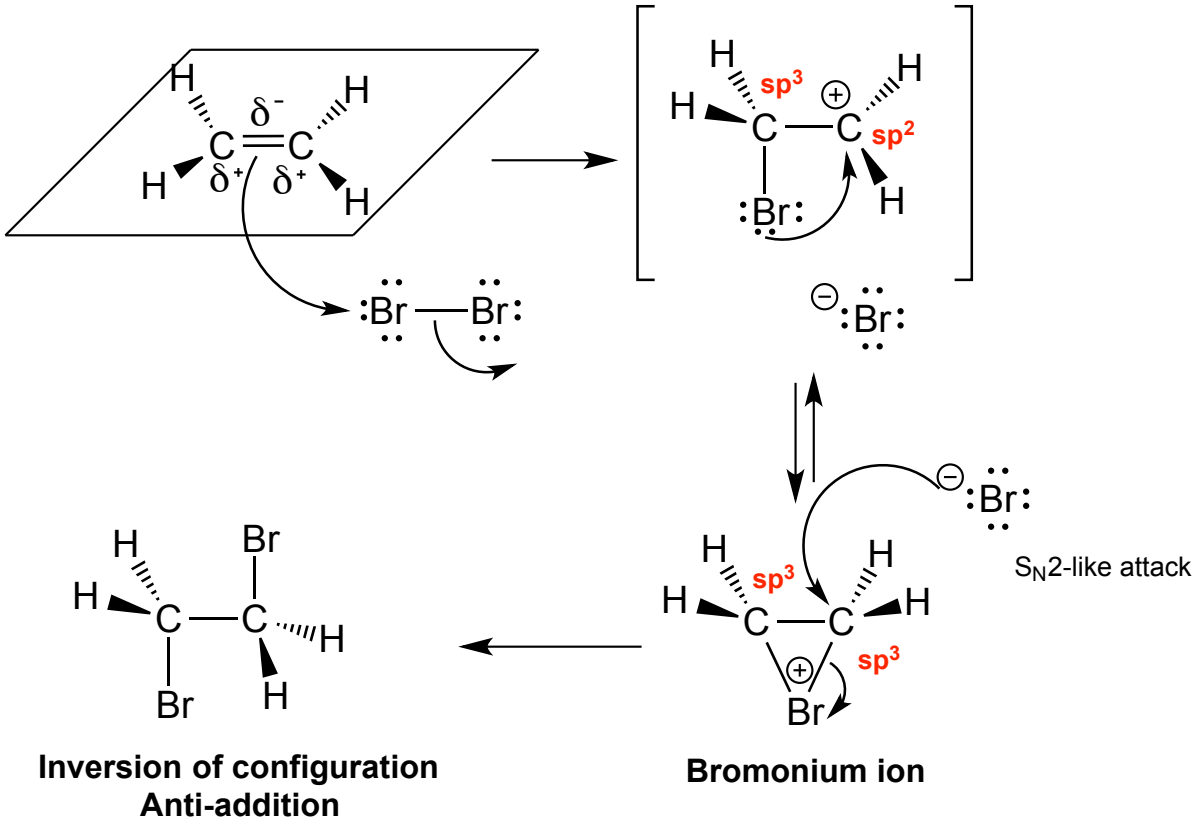


Cyclopentene

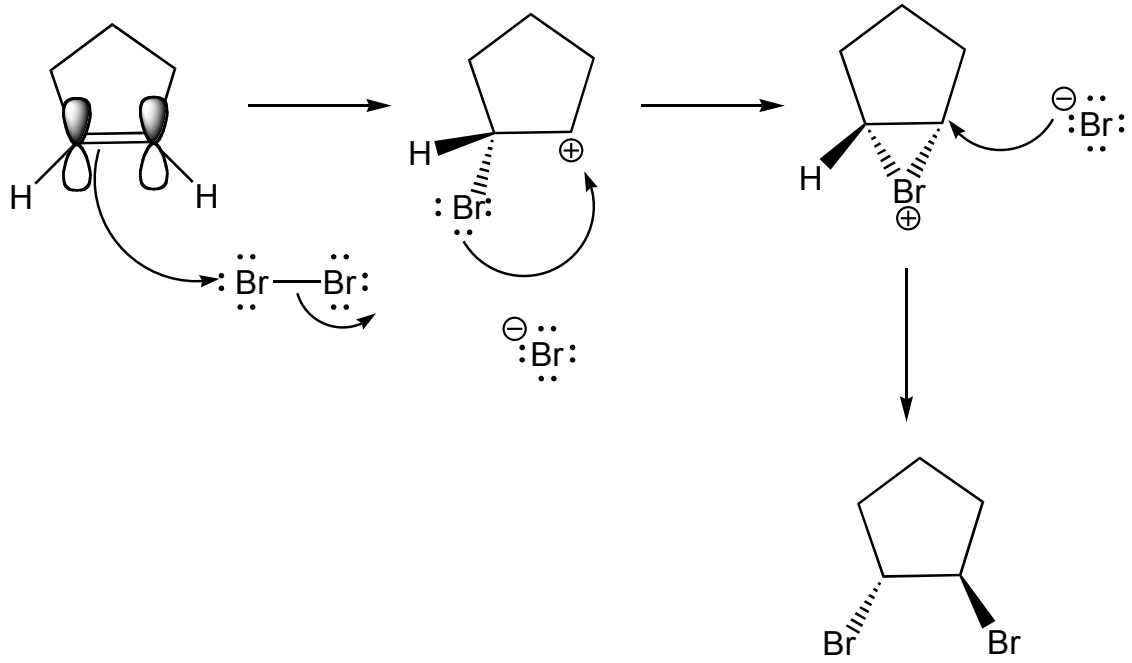


Mechanisms for the above reactions:

Alkene

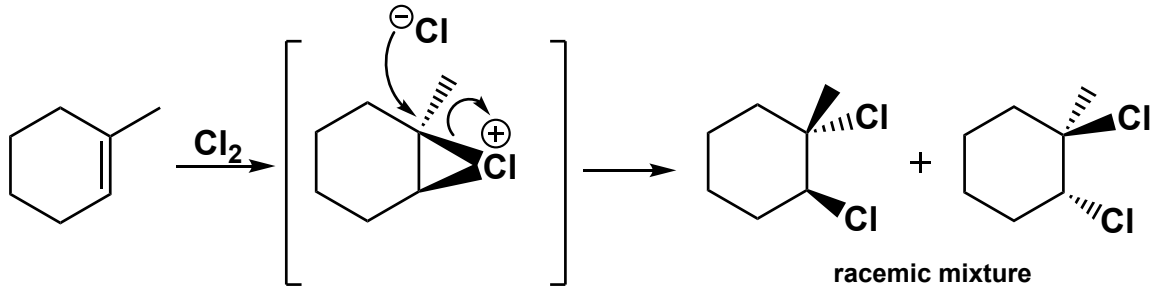


Cyclopentene



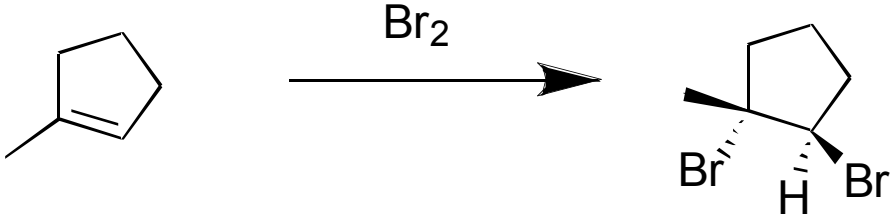
Trans-1,2-dibromocyclopentane

1-methylcyclohex-1-ene (*achiral*)

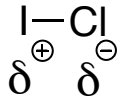


Additional examples for your reference:

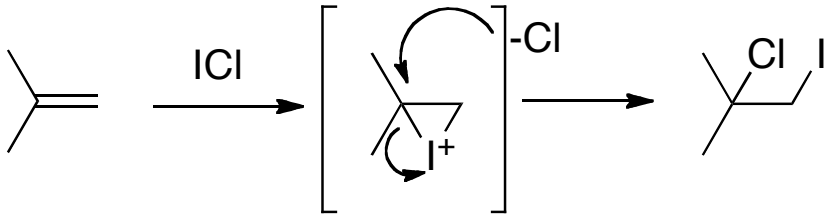
1.



2.



Iodine monochloride



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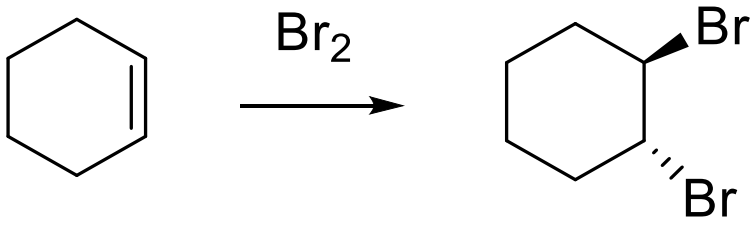

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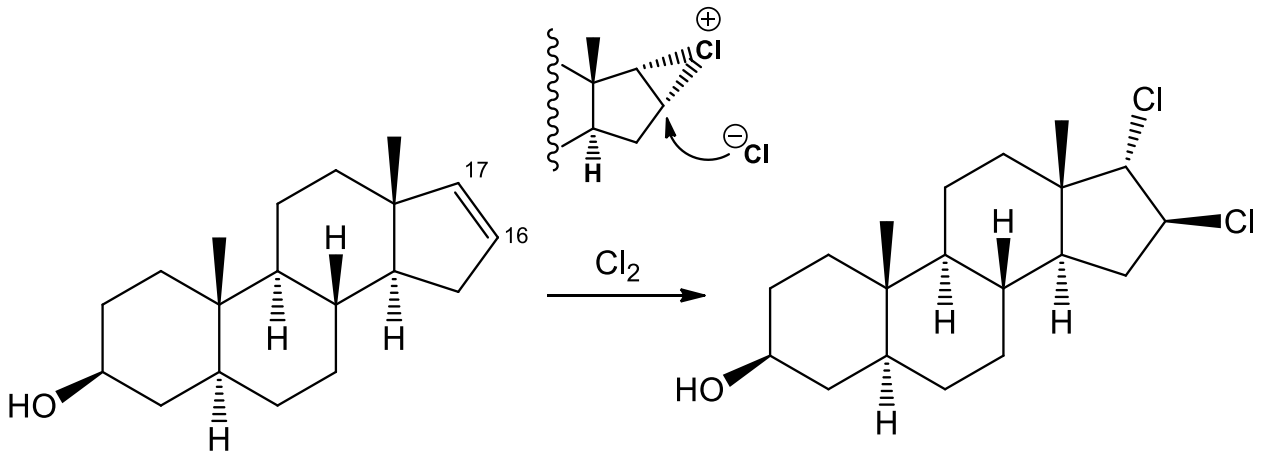
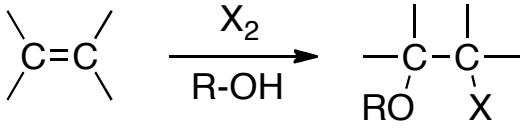


Reaction of Alkenes with Halogen and Water/Alcohol

General reaction

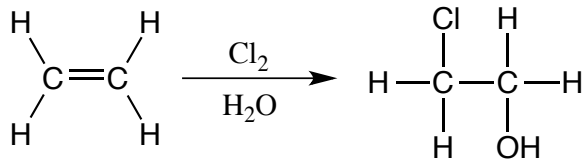


X = Cl, Br, F R = alkyl/H

Markovnikov's Rule

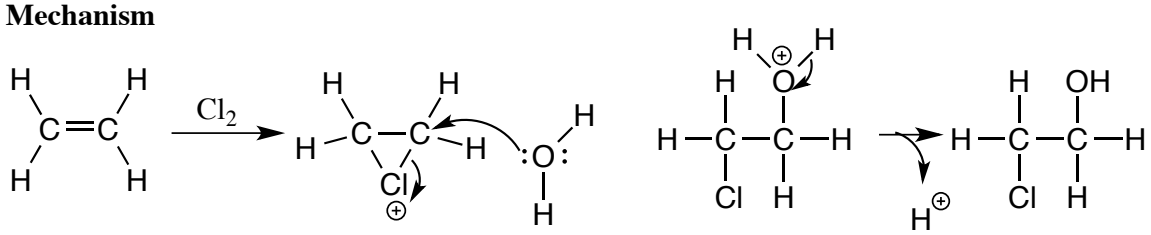
- positive species adds to the least substituted end of C=C
- negative species adds to the more substituted end of C=C (stabilized positive charge)

Example 1



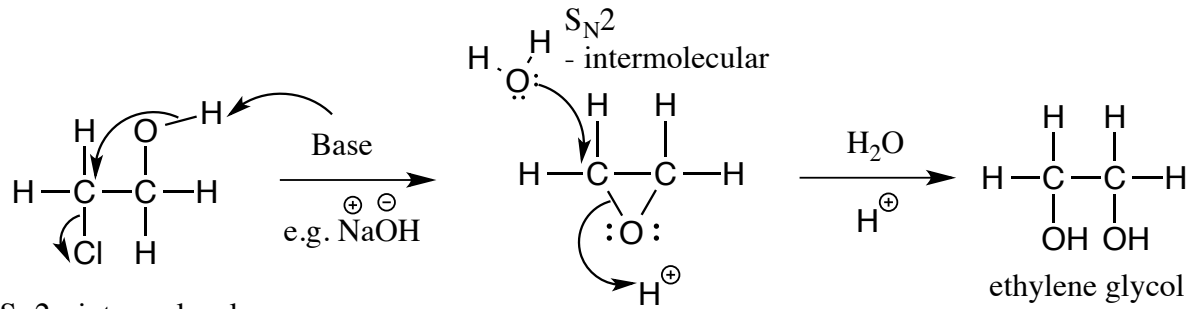
a chlorohydrin

Mechanism



Aside: Halohydrins are useful compounds for further reactions. The chlorohydrin below can be converted into an epoxide by an intramolecular (within a molecule) S_N2 reaction. The epoxide may then be converted into a 1,2-diol (intermolecular S_N2).

epoxide = oxirane = cyclic 3-membered ether

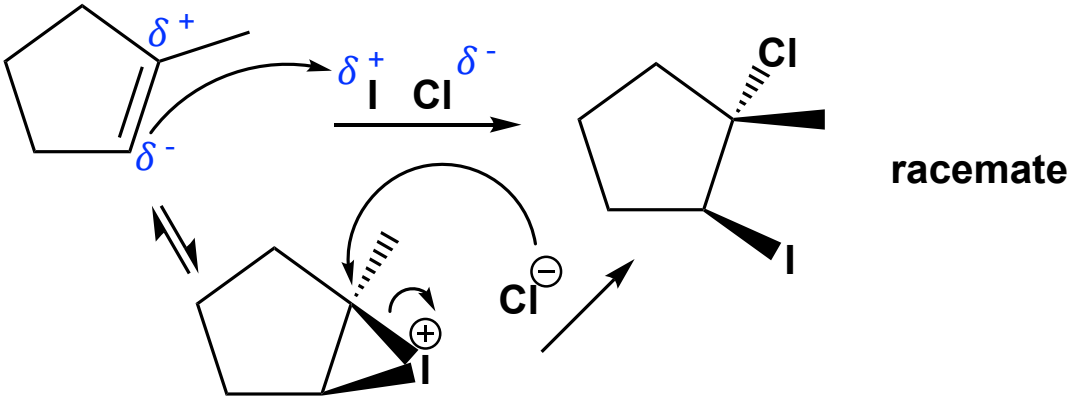


S_N2 - intramolecular
intramolecular rxns are FAST

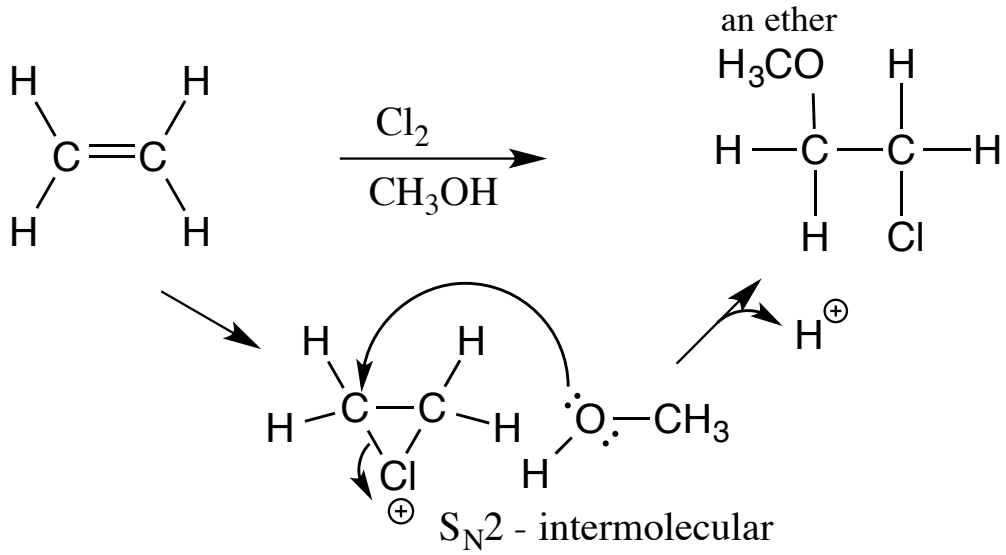
ethylene oxide
- reactive

ethylene glycol

Example 2

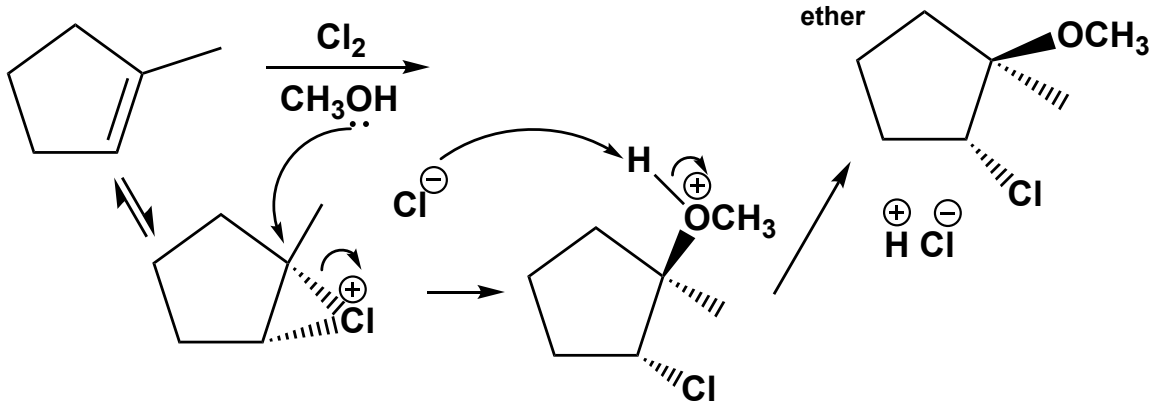


Example 3

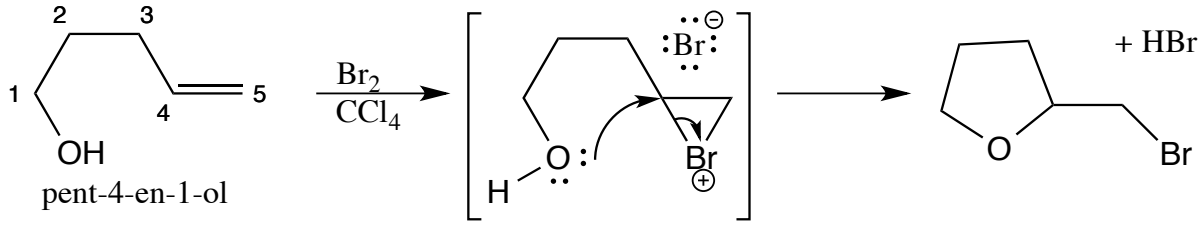


S_N2 - intermolecular

Example 4 (Markovnikov rule)



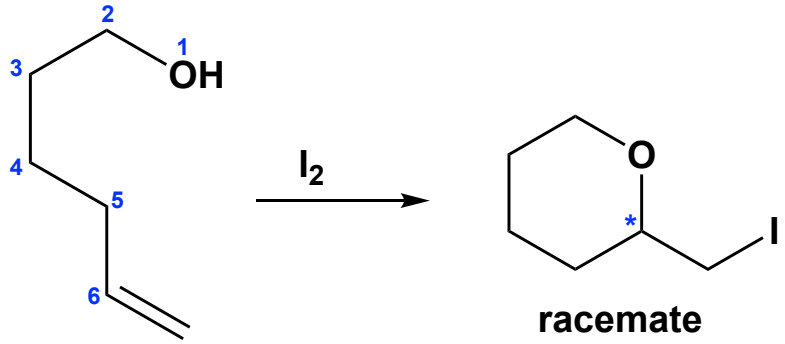
Example 5



Oxygen is a better nucleophile than bromide and **intramolecular** (within a molecule) cyclization is FAST. Product is a racemate

Can this reaction occur with chlorine? *Yes*. Iodine? *Yes*.

Example 6



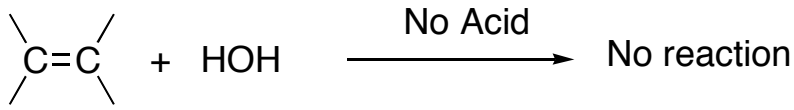
5-membered ring formation is favored → FAST
6-membered ring formation → OK, but much slower

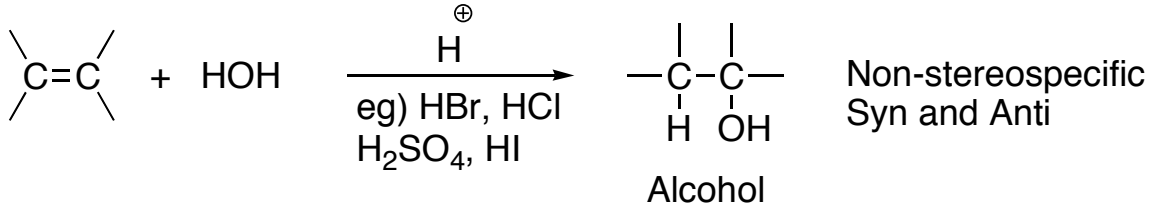
Terminology:
Intramolecular – within the same molecule
Intermolecular – amongst molecules

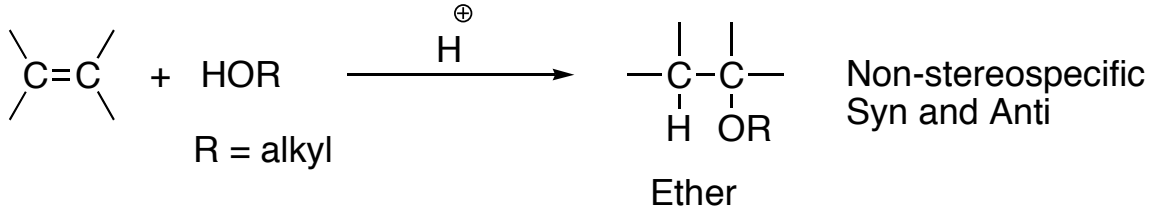
Hydration and Ether Formation

Addition of $\overset{\delta\oplus}{H}-\overset{\delta\ominus}{OH}$ or $\overset{\delta\oplus}{H}-\overset{\delta\ominus}{OR}$

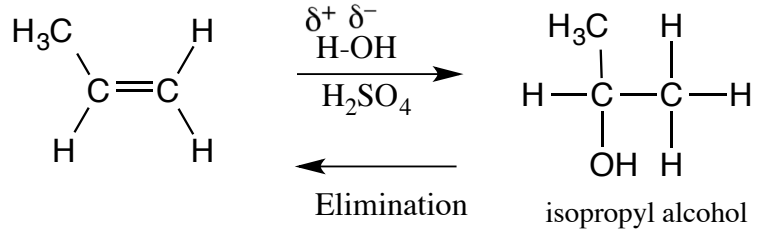
General Reactions:







Example 1 (follows Markvnikov's Rule)



Mechanism