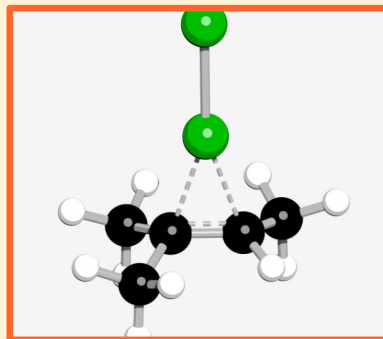


# HIGHLIGHTS

- Hydrohalogenation & hydration of alkenes
- Explanation of regioselectivity due to stability of carbocation (Markovnikov addition)
- Bromination
- Bromohydrin formation (& regioselectivity)
- Epoxidation with peracids
- *Syn*-dihydroxylation



Isolated alkenes are good nucleophiles. The reaction mechanism depends on the nature of the electrophile. Hydrohalogenation and hydration are the addition of H-X across the alkene. These additions proceed by a stepwise mechanism and are **regioselective** but **not** stereoselective. The regioselectivity is understood by considering the carbocation intermediate. This is sometimes known as **Markovnikov addition**. Bromination is also a stepwise reaction but is **stereospecific** (giving the **anti** product) but **not** regioselective. A modification of bromination allows the formation of bromohydrins or related compounds. The mechanism of the reaction is the same as bromination and is stepwise. It is stereospecific and regioselective. Epoxidation is a concerted reaction that occurs with **syn-addition**. It is stereospecific while regioselectivity is not an issue. *Syn*-dihydroxylation is essentially a concerted process that delivers *syn*-diols.

## CHEMISTRY CLASSICS

### $\pi$ NUCLEOPHILES PART I

### MARKOVNIKOV ADDITION OF ALKENES



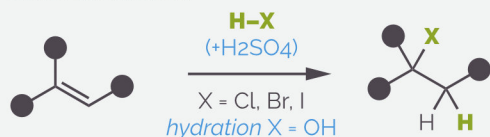
© gjr for makingmolecules.com  
This handout is shared under a  
Creative Commons Attribution-  
NonCommercial-ShareAlike  
BY-NC-ND-SA 4.0 licence.



# Alkenes as nucleophiles: Part 1

## 1. Addition of H-X

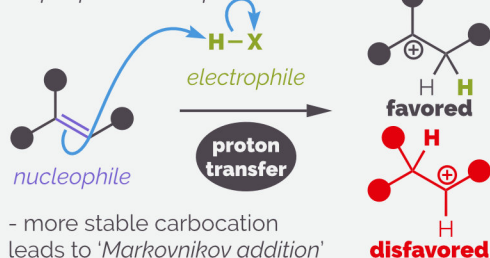
### General reaction



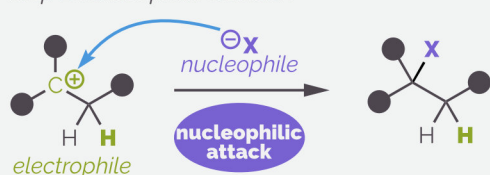
- control of **regiochemistry** (Markovnikov)
- no control of stereochemistry

### Mechanism

Step 1: proton transfer

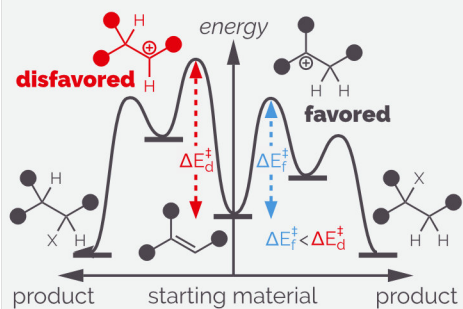


- more stable carbocation leads to 'Markovnikov addition'
- Step 2: nucleophilic addition

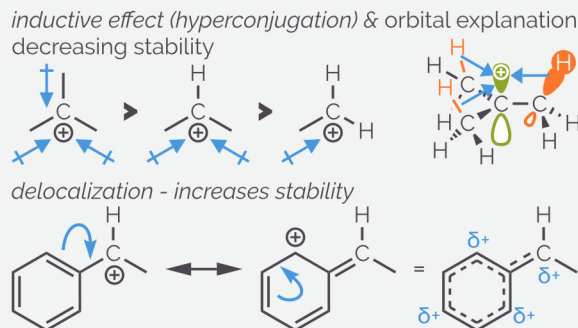


Step 3: proton transfer  
hydration requires a final deprotonation

## 2. Stability of carbocations: Regioselectivity

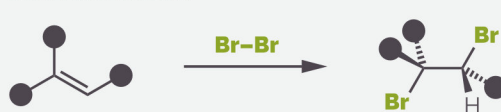


'Markovnikov addition' favors stable carbocation



## 3. Bromination

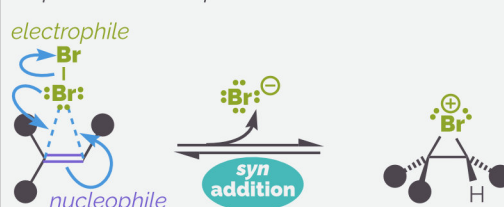
### General reaction



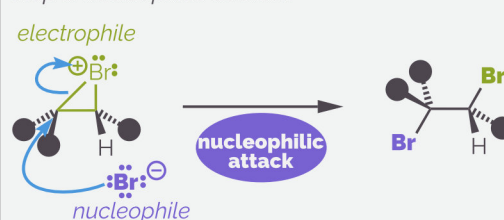
- regiochemistry not important
- control of **stereochemistry** (anti addition)

### Mechanism

Step 1: bromonium formation



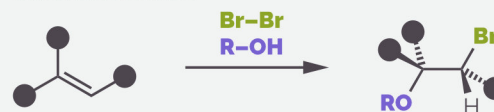
Step 2: nucleophilic addition



anti-addition due to ring opening bromonium ion orbitals align S<sub>N</sub>2-like substitution

## 4. Bromohydrins

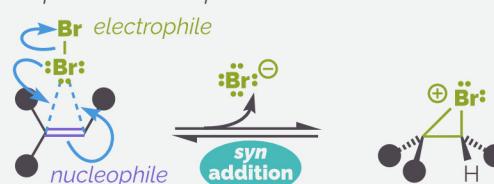
### General reaction



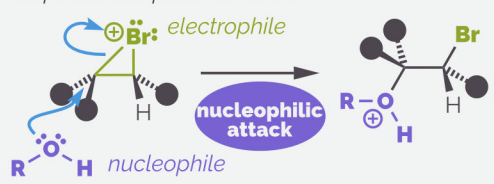
- control of **regiochemistry** (partial +ve)
- control of **stereochemistry** (anti addition)

### Mechanism

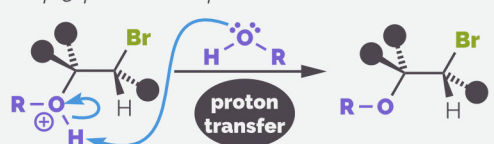
Step 1: bromonium formation



Step 2: nucleophilic addition

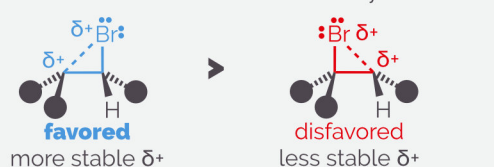


Step 3: proton transfer



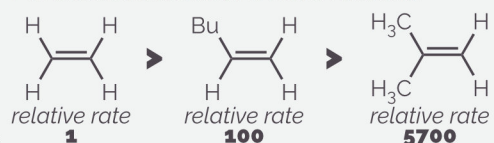
### Regioselectivity

Transition state favors  $\delta^+$  on tertiary carbon



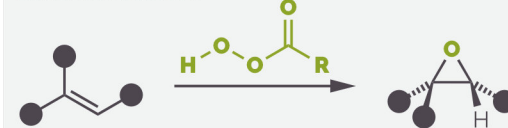
### Chemoselectivity

More substituted alkene more reactive.



## 5. Epoxidation

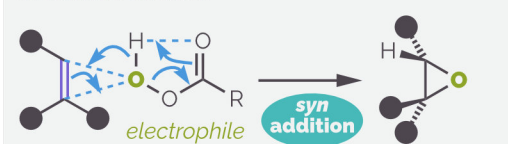
### General reaction



- regiochemistry not important
- control of **stereochemistry** (syn addition)

### Mechanism

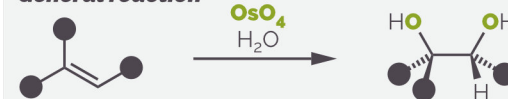
Concerted addition



Orbitals say this mechanism can't actually be right!

## 6. Syn-dihydroxylation

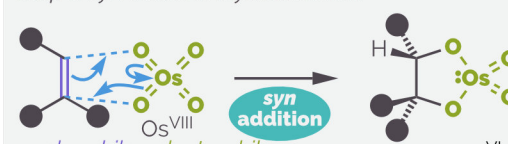
### General reaction



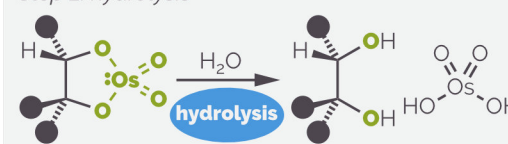
- regiochemistry not important
- control of **stereochemistry** (syn addition)

### Mechanism

Step 1: syn addition (cycloaddition)



Step 2: hydrolysis



### Catalytic variant (Upjohn reaction)

NMO re-oxidizes OsO<sub>4</sub> species

Use: OsO<sub>4</sub> (catalyst)  
H<sub>2</sub>O  
NMO

