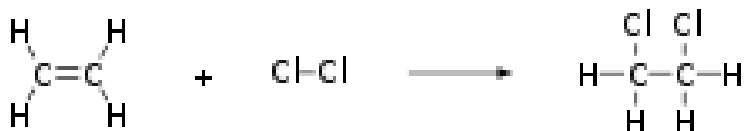


# STUDY OF REACTION MECHANISM: ADDITION REACTIONS

- A reaction in which one molecule combines with another to form a larger molecule with no other products
- A class of chemical reactions in which an atom or group of atoms is added to a molecule



- Addition reactions are reverse of Elimination reactions

## TYPES OF ADDITION REACTIONS

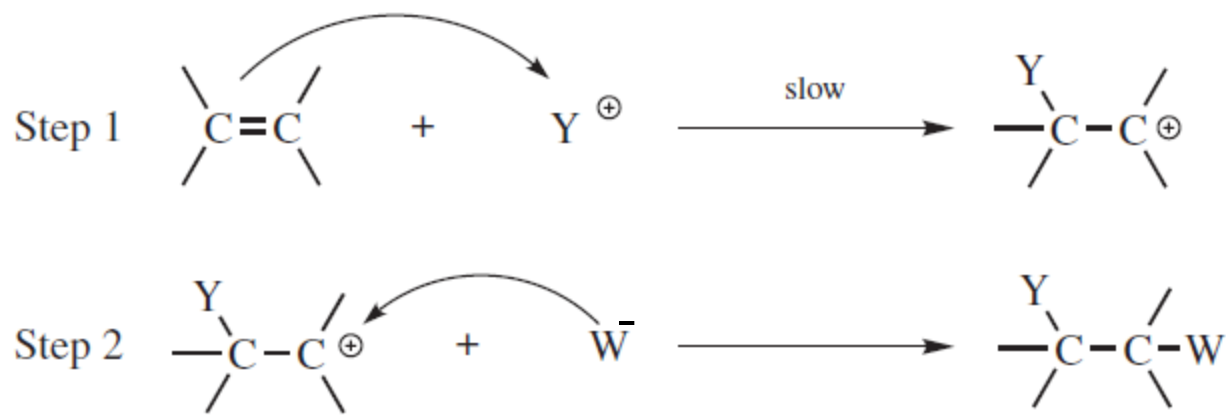
### 1. Addition to Carbon-Carbon Multiple Bonds

- Electrophilic Addition*
- Nucleophilic Addition*
- Free Radical Addition*
- Concerted or Simultaneous Addition*  
*Syn- vs anti- & 1,2- vs 1,4-Addtion*

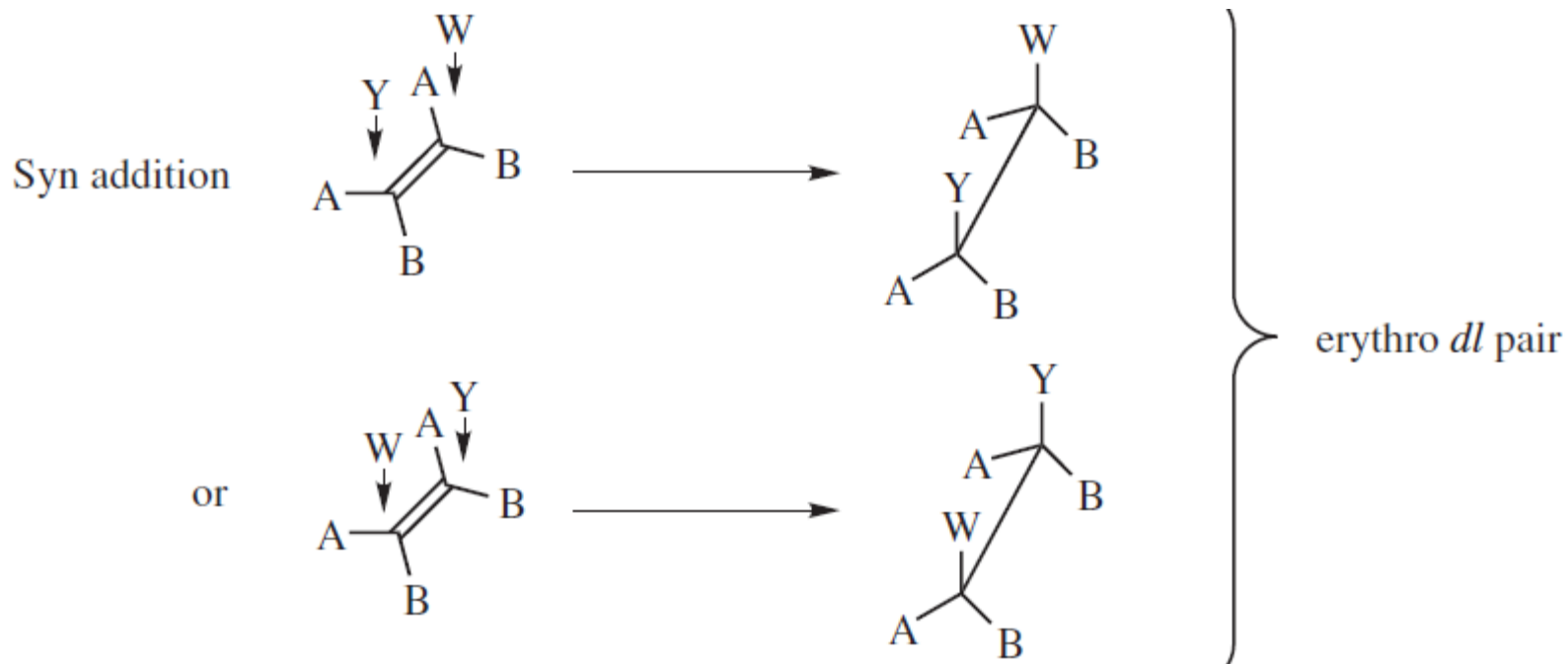
### 2. Addition to Carbon-Hetero Multiple Bonds

*Tetrahedral Mechanism*

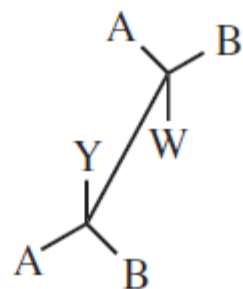
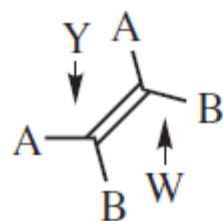
# Addition to Carbon-Carbon Multiple Bonds: *Electrophilic Addition*



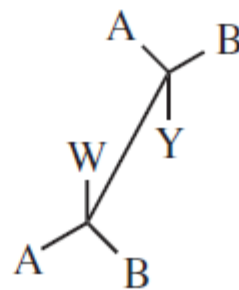
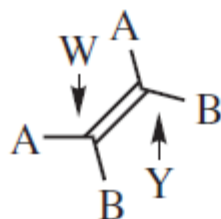
## *syn- vs anti-Addition*



Anti addition



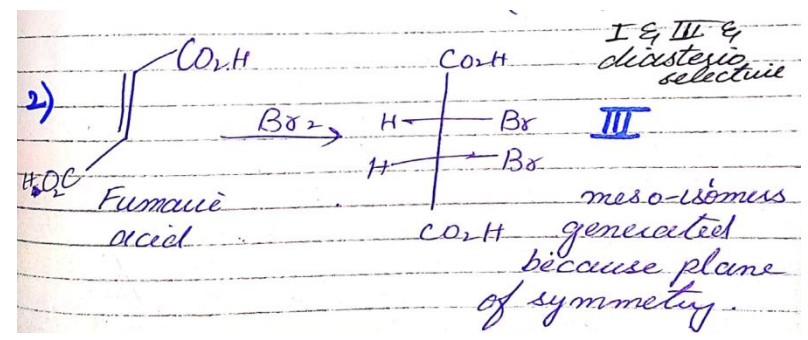
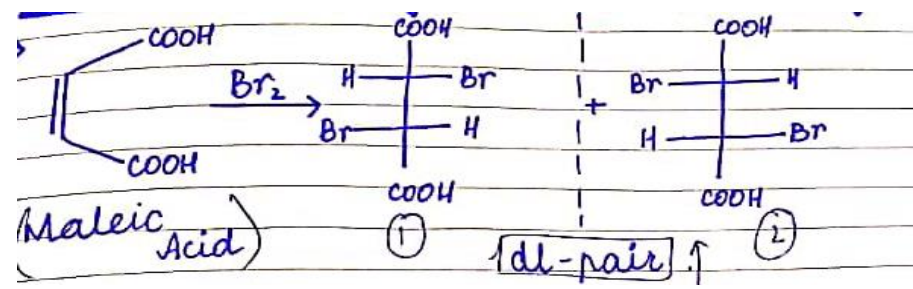
or



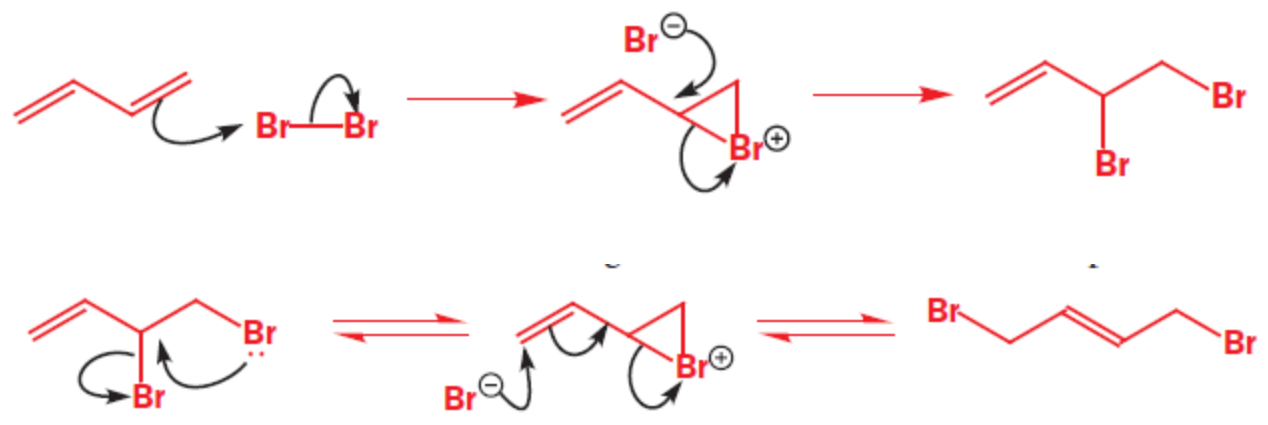
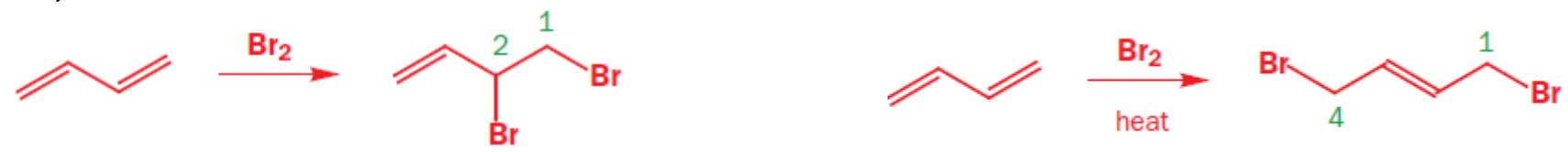
} three *dl* pair

# Example 1: Addition of Br<sub>2</sub>

- anti-Addition

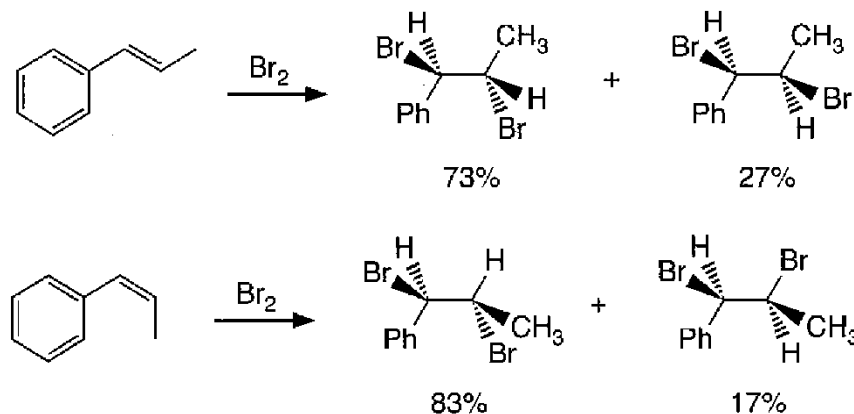
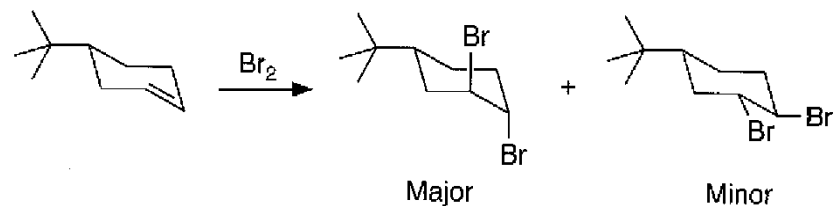


- 1,2- vs 1-4-Addtion



# Evidence for cyclic bromonium ion

## Stereochemistry

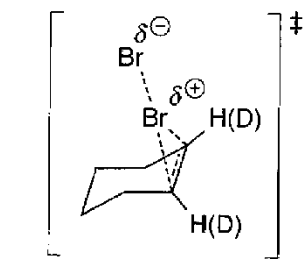


## Kinetics

Relative Rates for Addition of Bromine in Methanol with Added NaBr at 25 °C\*

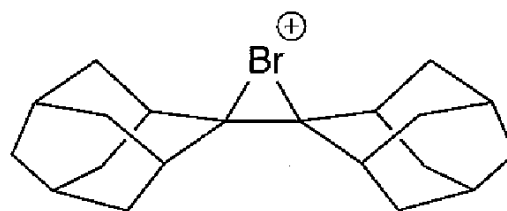
1	61	$1.7 \times 10^3$	$2.6 \times 10^3$	$5.4 \times 10^3$	$1.3 \times 10^5$	$1.8 \times 10^6$

## Kinetic Isotopic Effect



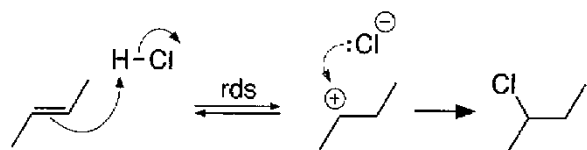
Bromination isotope effect

## Isolation

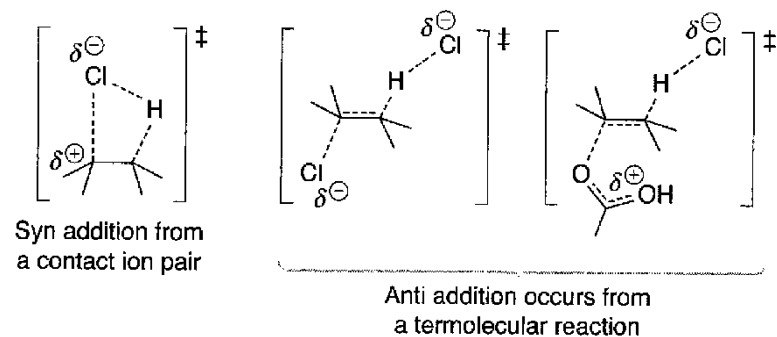
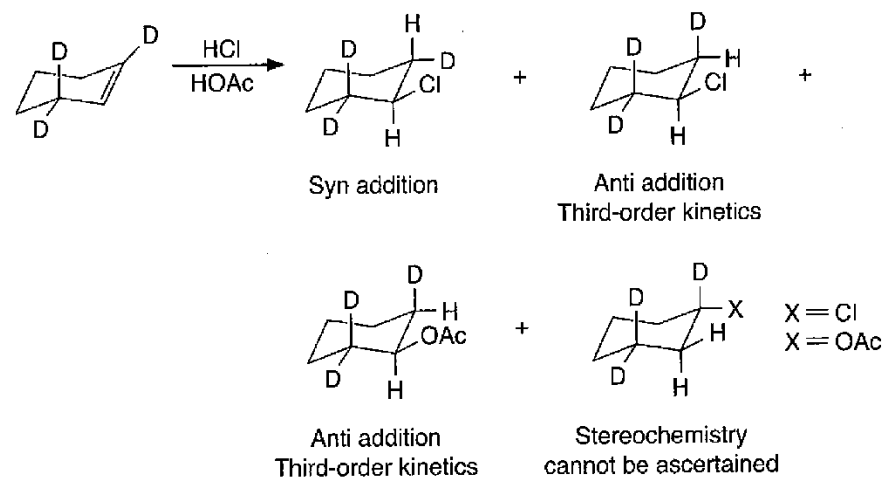
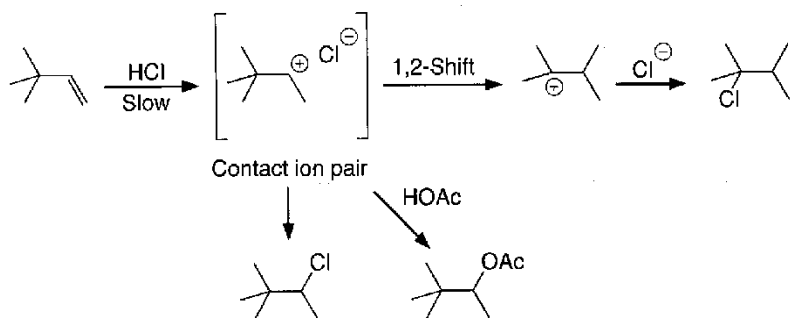
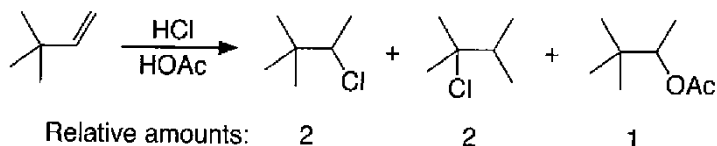


Stable bromonium ion

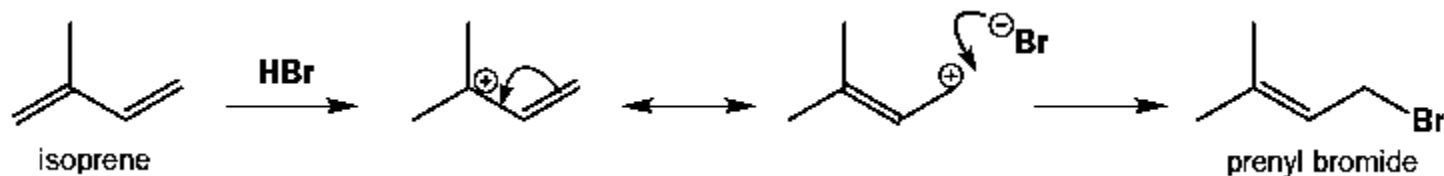
## Example 2: Addition of HX



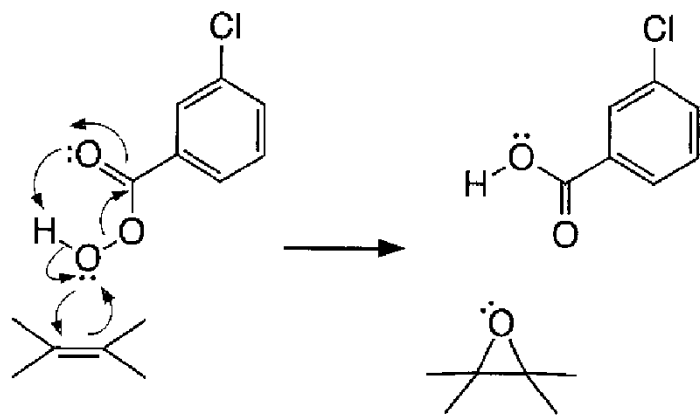
stereochemistry of HX addition is varied.  
predominant syn, anti, and nonstereoselective addition.



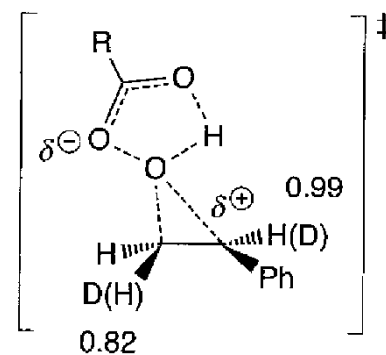
### • 1,2- vs 1-4-Addition



## Example 3: EPOXIDATION



### Isotopic Effect for Unsymmetrical T.S.



Unsymmetrical transition state

1. First order in alkene and first order in peracid
2. Hammett  $\sigma^+$  correlation yields  $\rho = -1.1$
3. Small Primary kinetic isotopic effect
4. Little dependence upon the solvent
5. Secondary deuterium isotopic effect
6. Butterfly mechanism