

# Alkenes II

## Electrophilic Addition Rxns

- Hydrohalogenation
- Halogenation
- Halohydrin Formation

Ref 8 : 1, 2, 12, 13

Prob 8 : 2a, 2c, 16, 17, 35, 36, 48

Adv Rdg 8 : 5 – 11

## General

### alkenes

- act as nucleophiles (base, ...)
- react w/ electrophilic reagents (Lewis acids, ...)
- undergo electrophilic add<sup>n</sup> rxns

complications: *regiochemistry?*,  
*stereochemistry?*

## Electrophiles

(Lewis acids;  $e^-$  sinks)

cmpds w/	Ex.
empty “AO”	
low energy empty $\sigma^*$ MO	

## 1.) Hydrohalogenation

(add<sup>n</sup> of HCl, HBr, HI ; usually in ether)

Overall:

Mech:

*regiochemistry: where will X go, left or right?*

## Regiochemistry

“X goes to the more substituted C”  
 (= Markovnikov’s Rule)

Ex.

- more stable carbocation formed in step 1
- recall  $\text{C}^+$  stability:

$3^\circ > 2^\circ > 1^\circ > \text{methyl}$

∴

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 hyperconjugation

### Illustration

- empty p orbital and C,C or C,H  $\sigma$  bond line up
- $\sigma$  bond feeds  $e^-$ ’s into empty p AO
- ∴ pos. charge spread;  
 cation stabilized

## Stability due to Hyperconjugation

aside on:

### conjugation

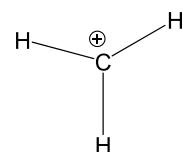
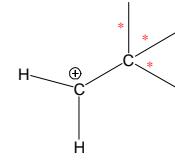
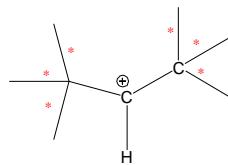
= “interaction between adjacent p orbitals”  
 e.g.,

### hyperconjugation in carbocations:

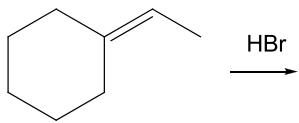
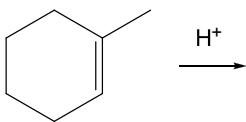
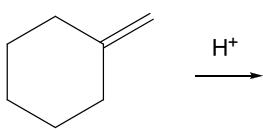
= sideways overlap  
 between “empty p orbital”  
 and “ $\sigma$  bond on adjacent C”  
 “spreads pos. charge, makes cation more stable”

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 hyperconjugation

- the more adjacent  $\sigma$  bonds, the more stable



Practice



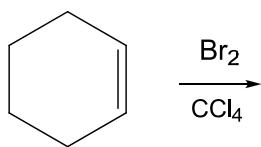
Detailed Mech.

## 2.) Halogenation

Add<sup>n</sup> of  $\text{X}_2$  in a non-nucleophilic solvent,  
esp.  $\text{CCl}_4$

Detailed Mech.

## Example



## Halohydrin Formation

“Halogenation in  $\text{H}_2\text{O}$ ”

## Detailed Example

## Practice

