Alkenes II

Electrophilic Addition Rxns

- Hydrohalogenation
- Halogenation
- Halohydrin Formation

Ref 8 : 1, 2, 12, 13

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

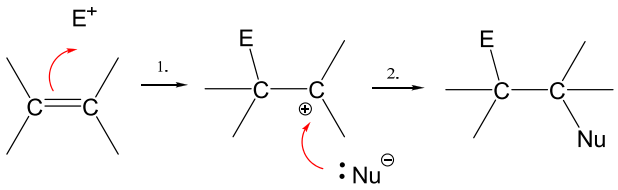
7 : 7, 18 – 21 (alkynes for later)

Adv Rdg 8 : 5 – 11

General

alkenes

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



complications: *regiochemistry?*, *stereochemistry?*

Electrophiles

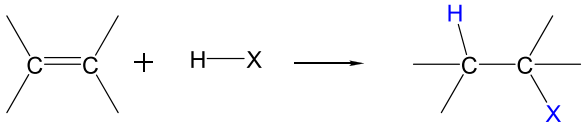
(Lewis acids; e^- sinks)

cmpds w/	**Ex.**
empty "AO"	BH_3 carbocation, metal cation, H^+, H_3O^+
low energy empty σ* MO	H-Br, Br - Br

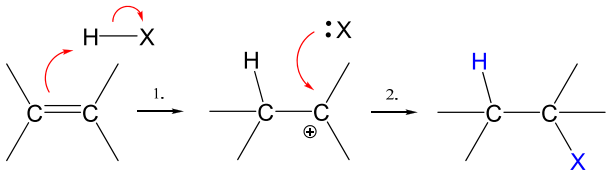
1.) Hydrohalogenation

(add^n of HCl, HBr, HI , usually in ether)

Overall:



Mech:

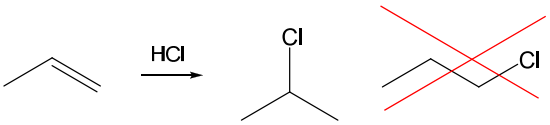


regiochemistry: where will X go, left or right?

Regiochemistry

" X goes to the more substituted C"
(= Markovnikov's Rule)

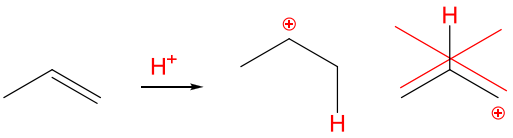
Ex.



• more stable carbocation formed in step 1
• recall C^+ stability:

3° > 2° > 1° > methyl

∴

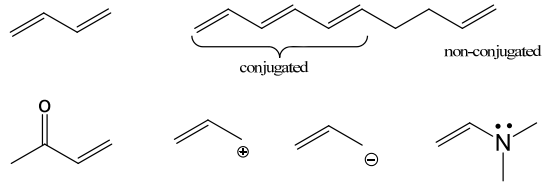


Stability due to Hyperconjugation

aside on:
Conjugation

= "interaction between adjacent p orbitals"

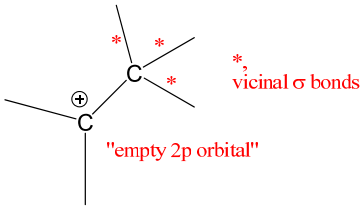
e.g.,

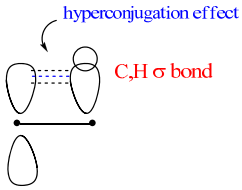


hyperconjugation in carbocations:
= sideways overlap
between "empty p orbital"
and "σ bond on adjacent C"
"spreads pos. charge, makes cation more stable"

hyperconjugation

Illustration



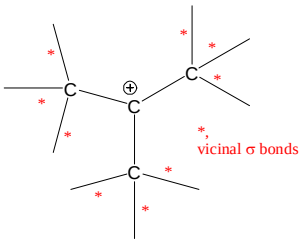


• empty p orbital and C,H σ bond line up
• σ bond feeds e^-'s into empty p AO

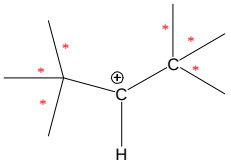
∴ pos. charge spread;
cation stabilized

hyperconjugation

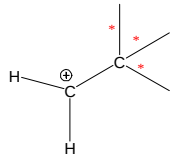
• the more adjacent σ bonds, the more stable



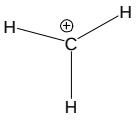
3°,
9 adjacent σ bonds



2°,
6 adjacent σ bonds

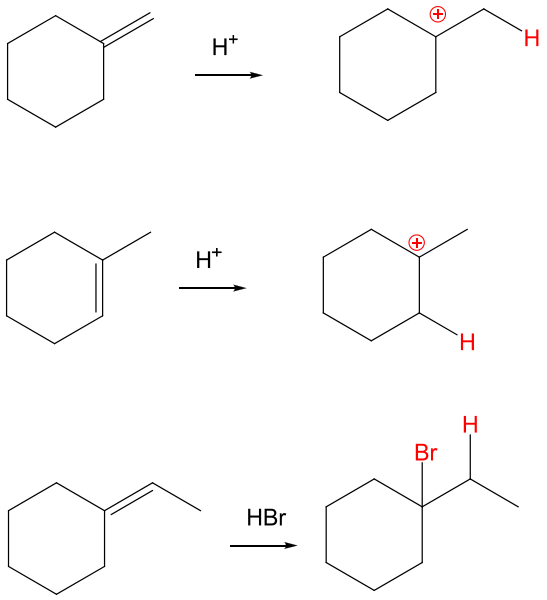


1°,
3 adjacent σ bonds



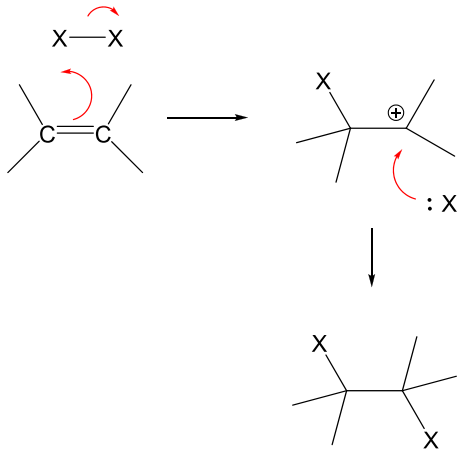
methyl,
no hyperconjugation

Practice



2.) Halogenation

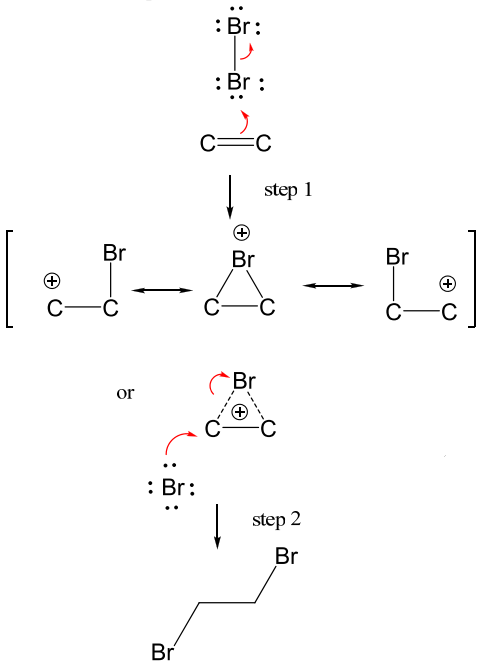
Add X_2 in non-nucleophilic solvent, esp. CCl_4



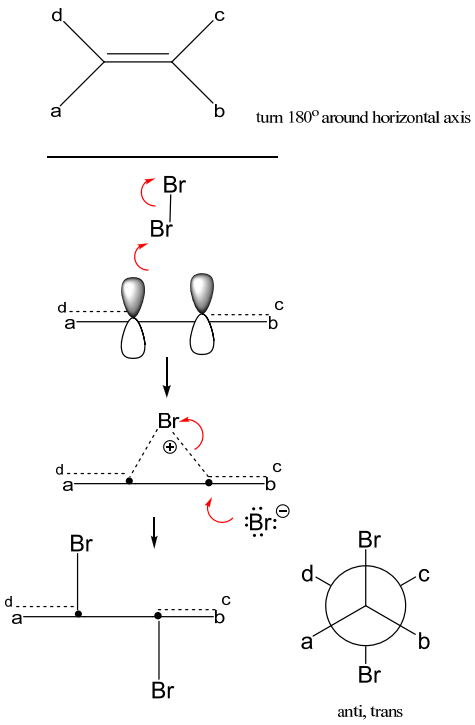
Note: X – X can act as electrophile,
b/c it has a low energy empty σ* MO

Detailed Mech.

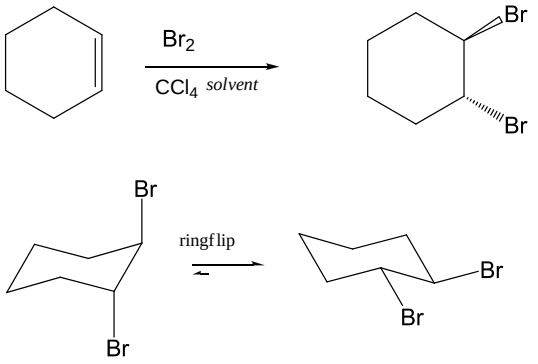
somewhat more complicated



Detailed Mech., to show trans stereochemistry:



Example



trans product,

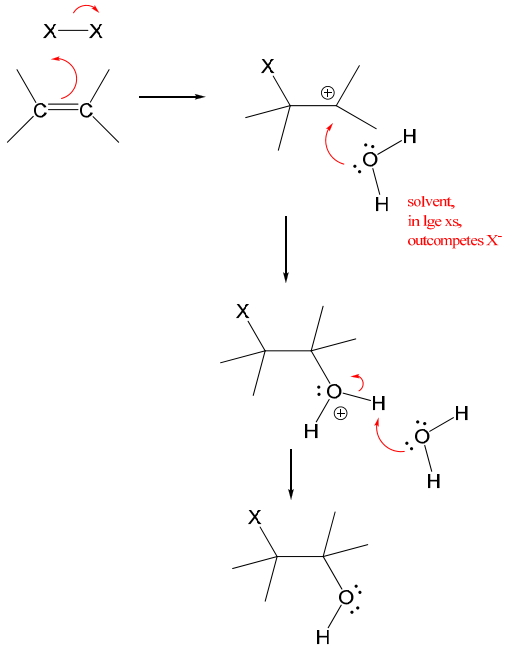
1 diastereomer only,

chiral, but racemic

Halohydrin Formation

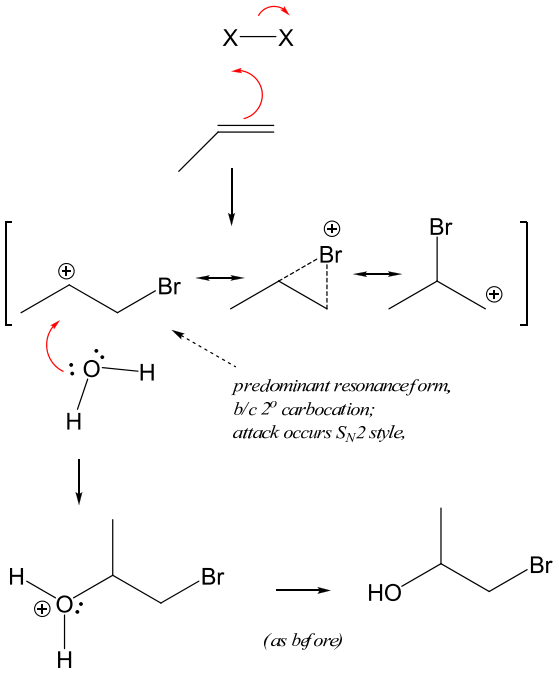
"Halogenation in H_2O"

overall: addition of –OH and –X



"halohydrin"

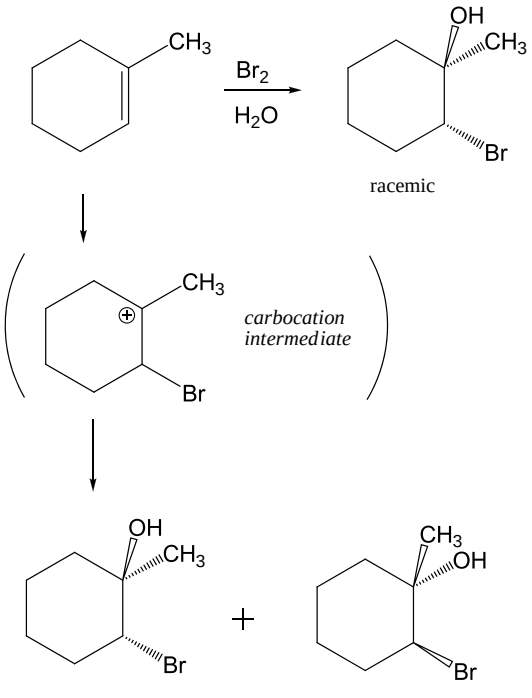
Detailed Specific Example



Notes: –OH goes to more substituted C;

Br, OH added trans, although cannot be detected here;
but see Practice Example

Practice



enantiomers