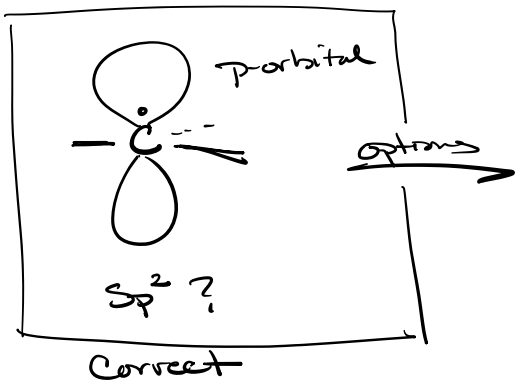
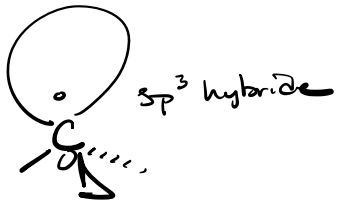
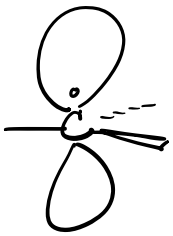
Free Radical

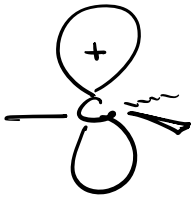




sp^3 ?



Free Radical is electron dificient



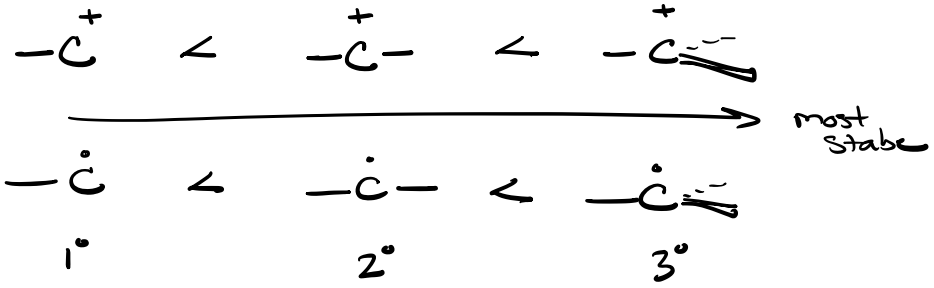
Carbocation

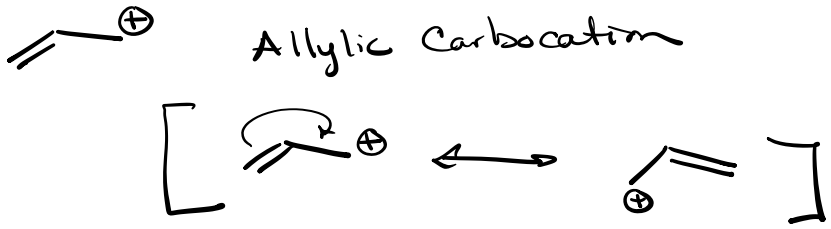
Structurally Similar

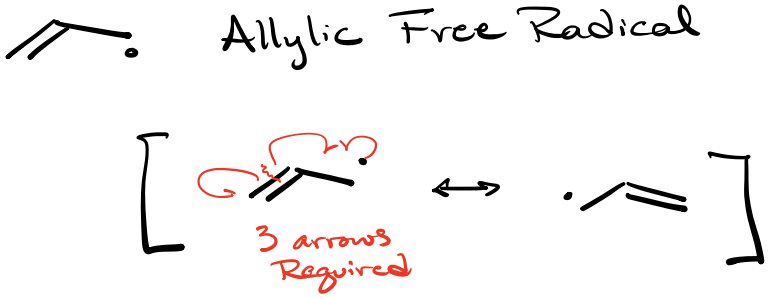
Similar Stability issues

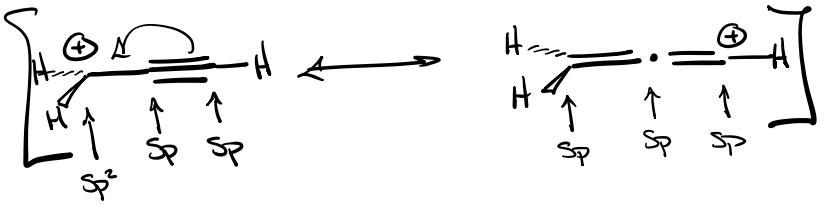
more substituted = more stable

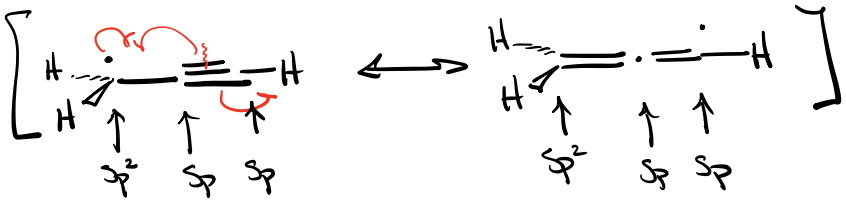
more resonance = more stable



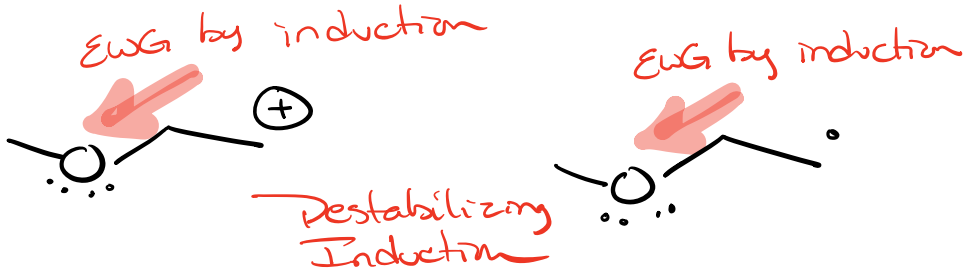

Allylic Carbocation


Allylic Free Radical
3 arrows Required

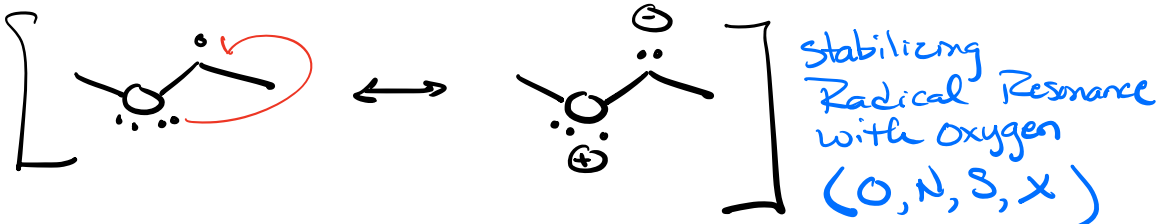

sp²
sp
sp
sp
sp
sp


sp²
sp
sp
sp²
sp
sp

* Key Difference

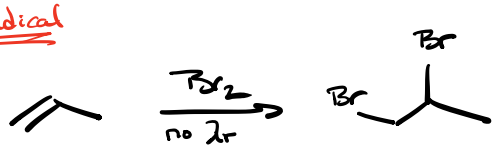


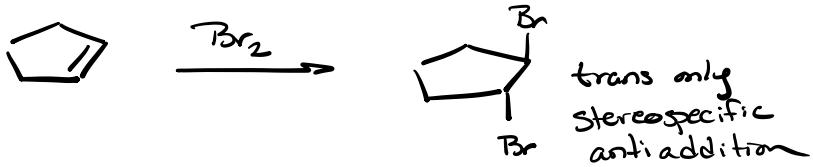
Instead



Halogenation Br_2, Cl_2

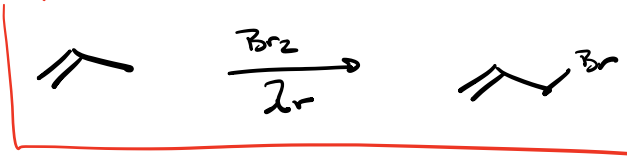
Not Free Radical





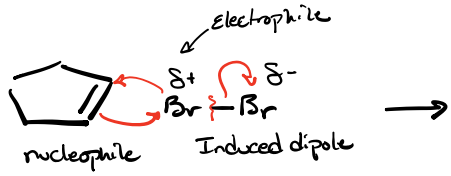
trans only
stereospecific
anti addition

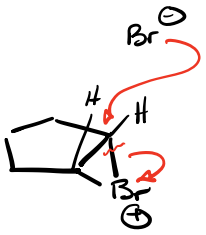
* Free Radical



Come back to later

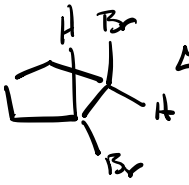
Mechanism



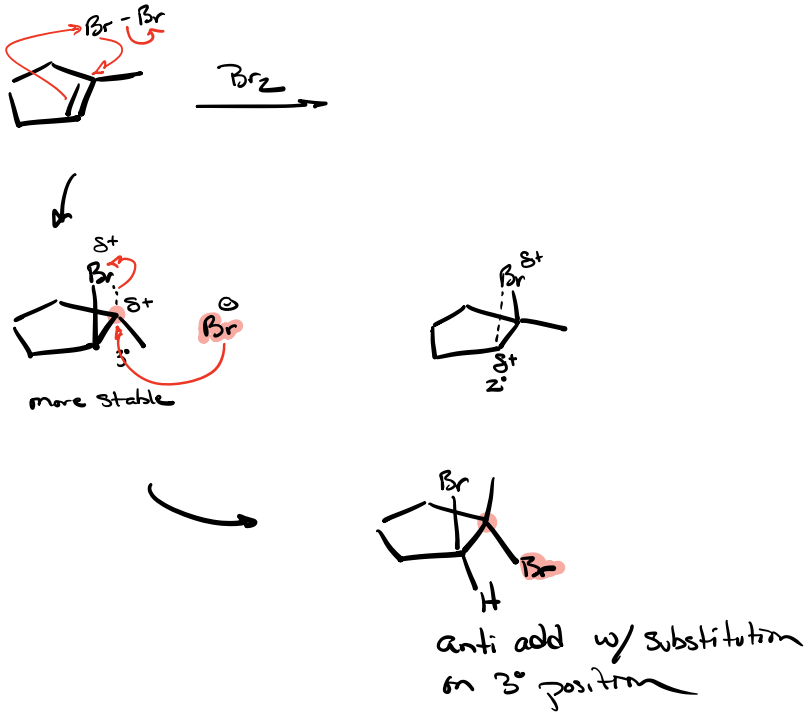


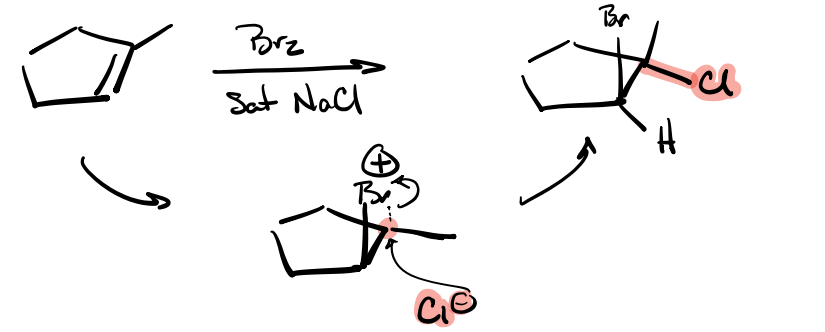
Cyclic Bromonium ion

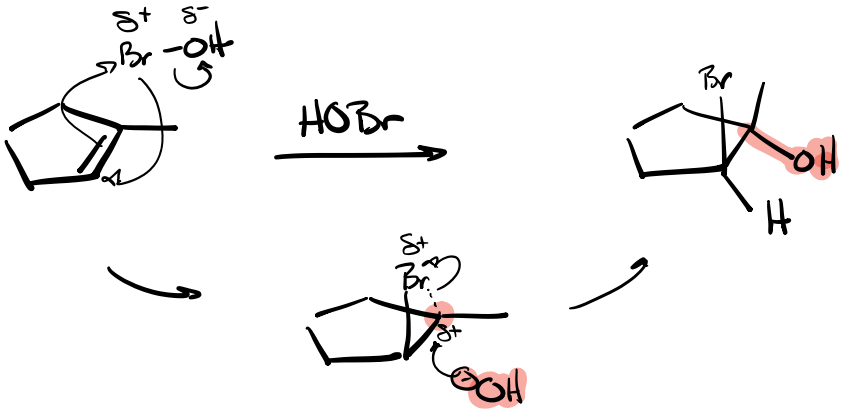
S_N2
Backside attack

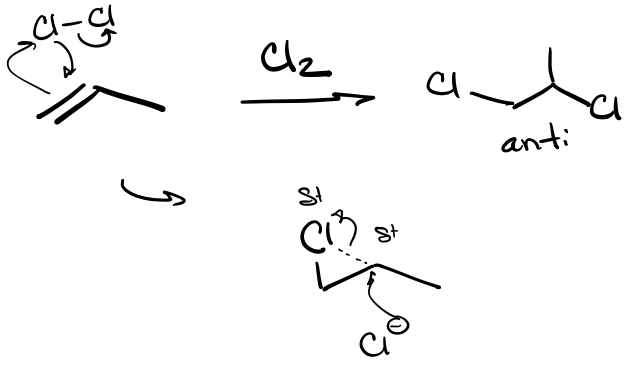


anti add


Br - Br
Br2
δ+
Br
δ+
Br
more stable
δ+
Br
δ+
anti add w/ substitution
on 3° position


Br2
Sat NaCl
Br
Cl
H
Br
Cl


δ+
Br
δ-
OH
HOBr
Br
OH
H
δ+
Br
δ+
OH

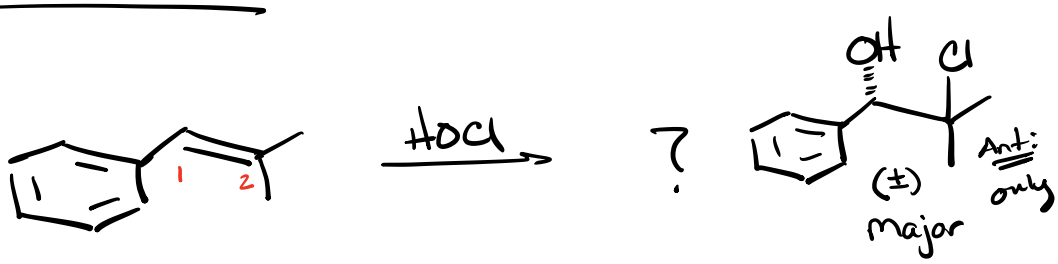


Size

Bromine can span better

Chlorine is more selective than bromine for second incoming nucleophile

Question

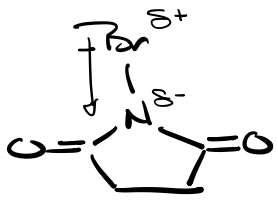


Resonance Benzylic

more stable

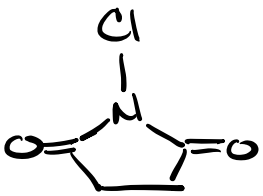
Inductive 3°

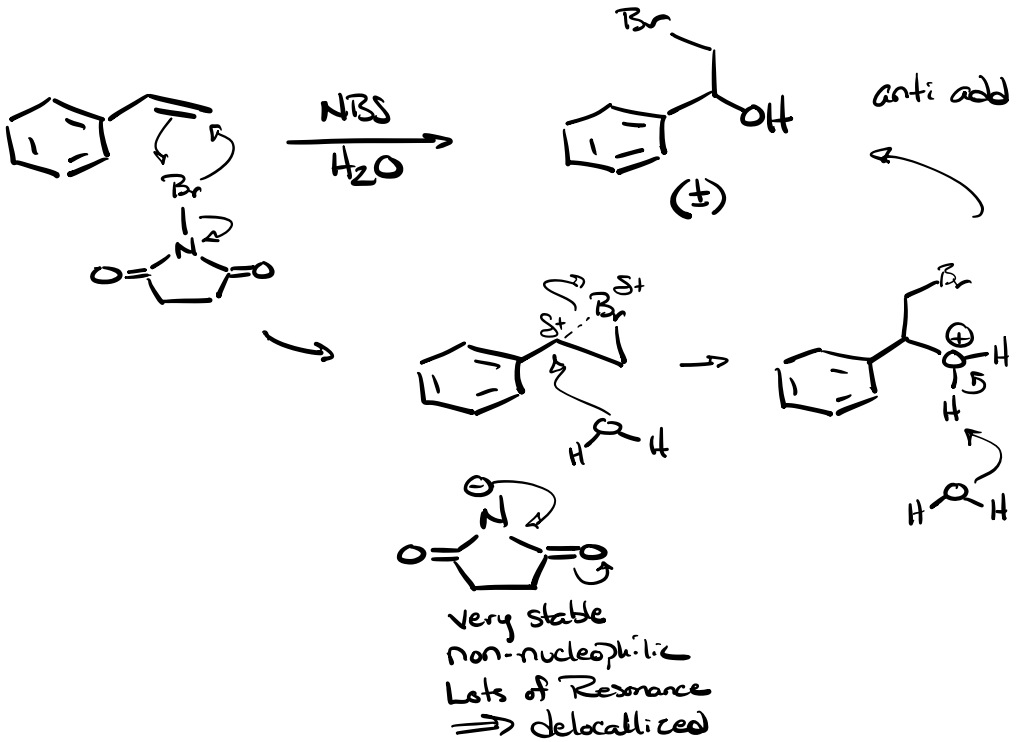
N-Bromo Succinamid (NBS)



Electrophilic Source of halogen

N-Chloro Succinamide (NCS)

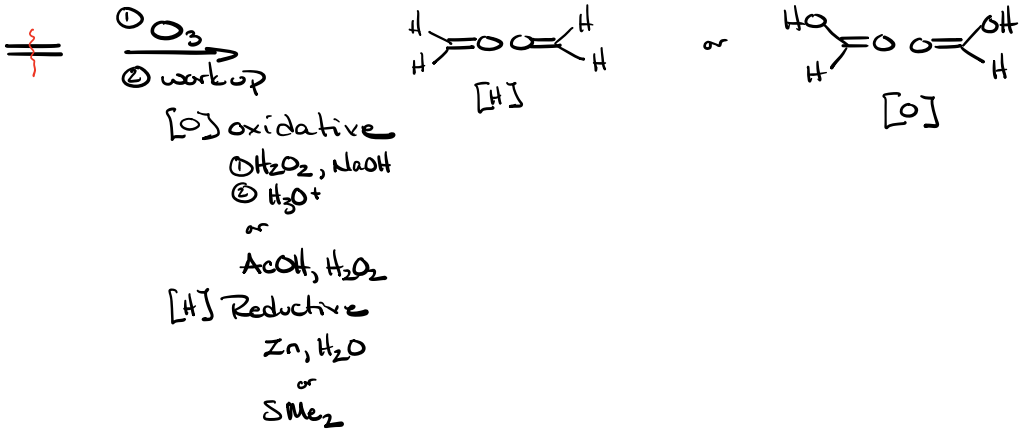


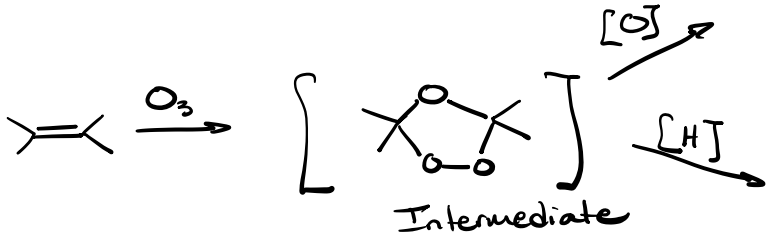


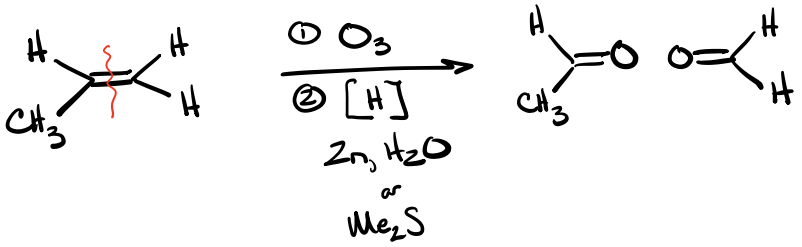
* Addition of Br and Cl go by cyclic halogen ion and second nucleophile attacks anti at more stable δ+ (Resonance > Induction)

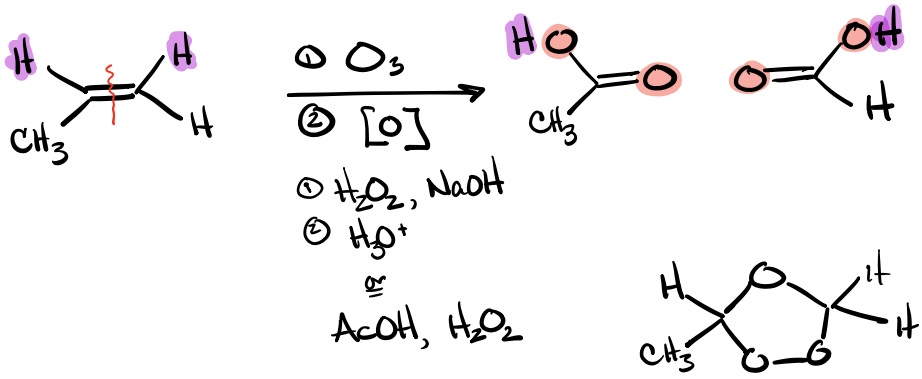
F	too small, too electron withdrawing
Cl, Br	for Carbon: Size of orbitals & electronegativity
I	too large
At	?

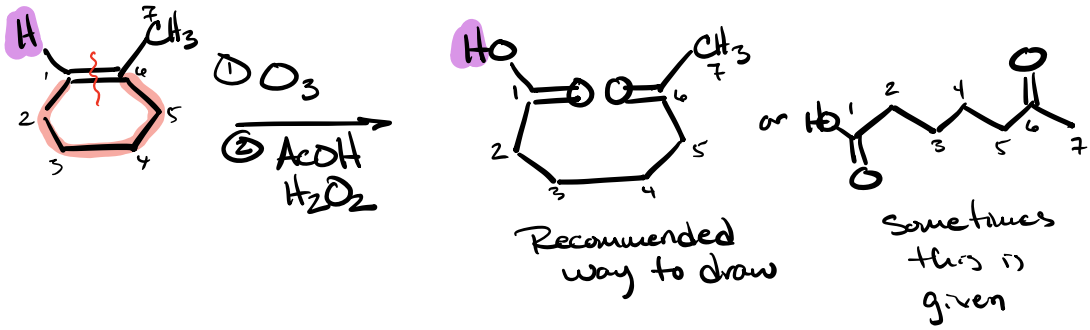
Ozonolysis

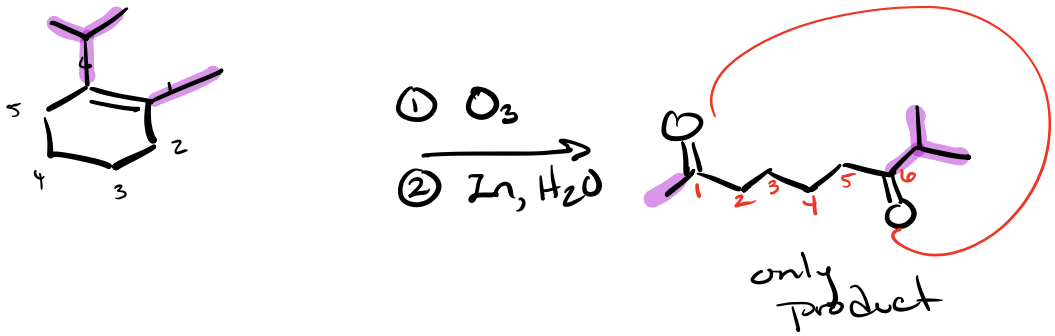





① O3
② [H]
Zn, H2O
or
Me2S


① O3
② [O]
① H2O2, NaOH
② H3O+
or
AcOH, H2O2


① O3
② AcOH
H2O2
Recommended way to draw
or
Sometimes this is given


① O3
② Zn, H2O
only product