

Overheads: - Outline

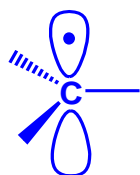
Recap Friday:

## I) Radical Halogenation

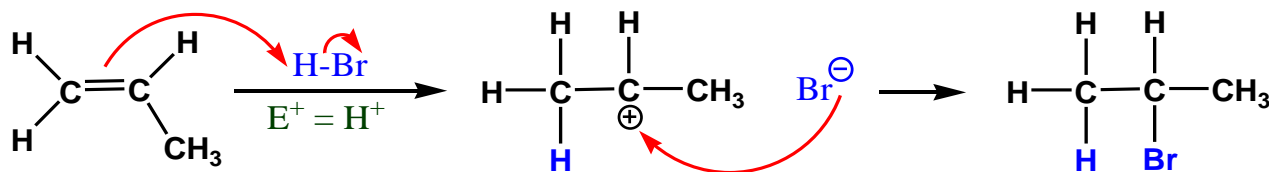
Selectivity: Ratios result from:

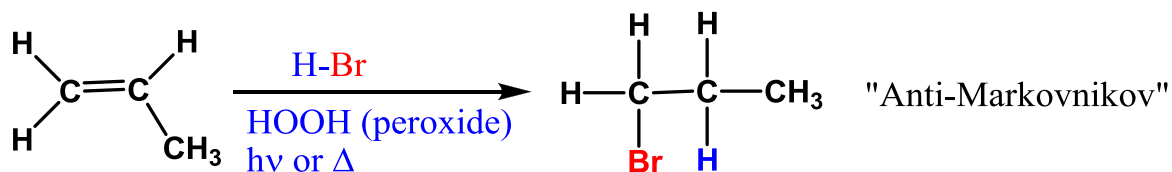
- 1) # of each type of H
- 2) Halogen radical being used  
 $\text{Br}\cdot$  is more stable than  $\text{Cl}\cdot$   $\therefore$  it is more selective  
 $\therefore$  get more  $3^\circ$  for Br than Cl
- 3) Relative stabilities of carbon radicals  
 Resonance  $> 3^\circ > 2^\circ > 1^\circ$

\*\* for allylic halogenations of alkenes use NBS to avoid EA

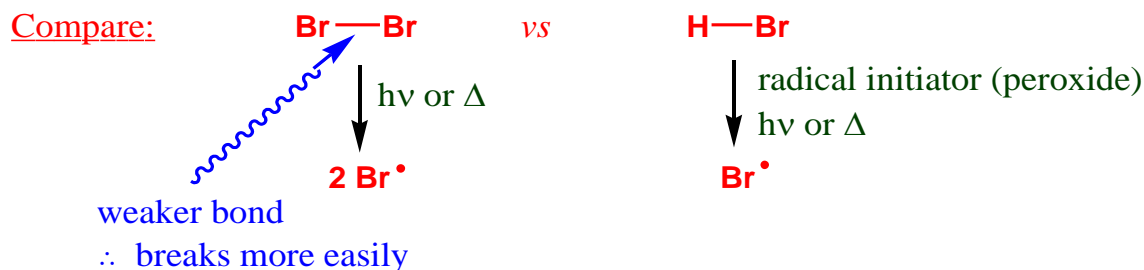
NOTE: Only  $\text{C}^+$  can rearrange, so once formed radical does NOT rearrangeStereochemistry of Radical Halogenation (and all radical reactions)

- radical is flat ( $\text{sp}^2$ ) - like  $\text{C}^+$
- $\text{Br}_2$  can add to either top or bottom (like  $\text{C}^+$ )

 $\therefore$  reaction is not stereoselective! $\Rightarrow$  if a chiral center is formed, usually get racemic product (50:50 R:S)II) Radical Addition of H-Br to Alkenes: second radical reaction"Normal" Addition of H-Br:Markovnikov:  $\text{H}^+$  ( $=\text{E}^+$ ) adds to end with most H's $\Rightarrow$  What if we want the Br to go to the end with the most H's? $\Rightarrow$  we need the Br to be the  $\text{E}^+$ !How? Radicals!  $\text{Br}\cdot = \text{E}^+$  (only has 7  $\text{e}^-$ )

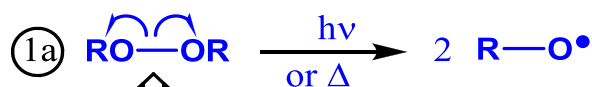


⇒ Need to add radical initiator (such as HOOH or ROOR) to make Br• from H-Br

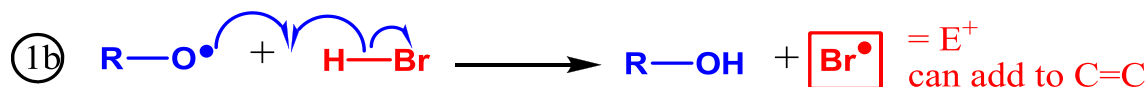


Mechanism:

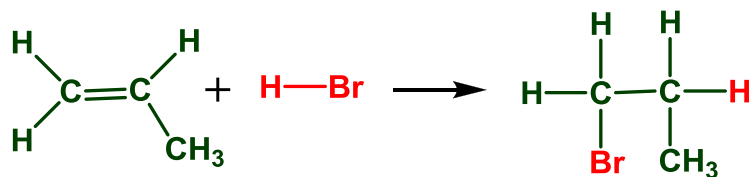
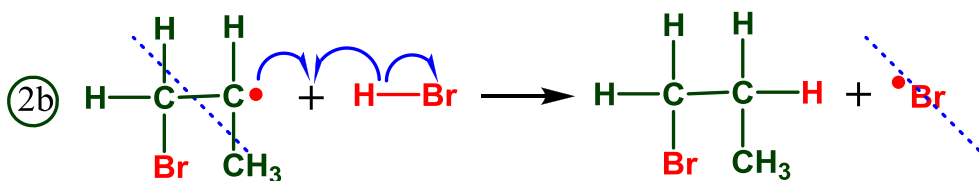
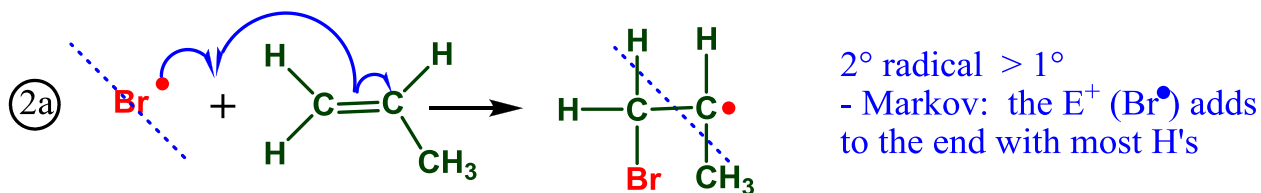
Initiation



O-O bond weak, like Br-Br ∴ breaks easily  
 \*\*\*only add small amount to initiate reaction

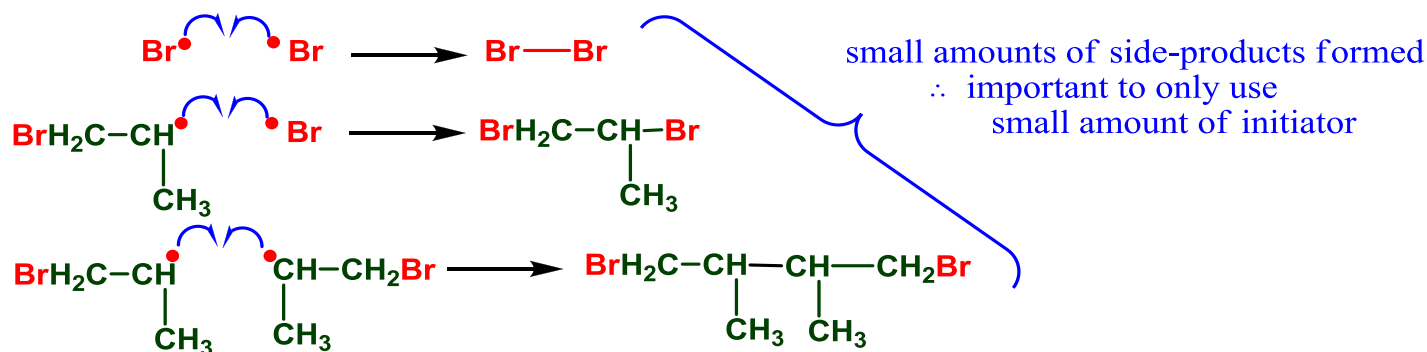


Propagation



- called "Anti-Markovnikov" because "backwards", but really still follows Markov since Br• = E<sup>+</sup>

③ Termination: any 2 radicals combine



⇒ Works for H-Br only

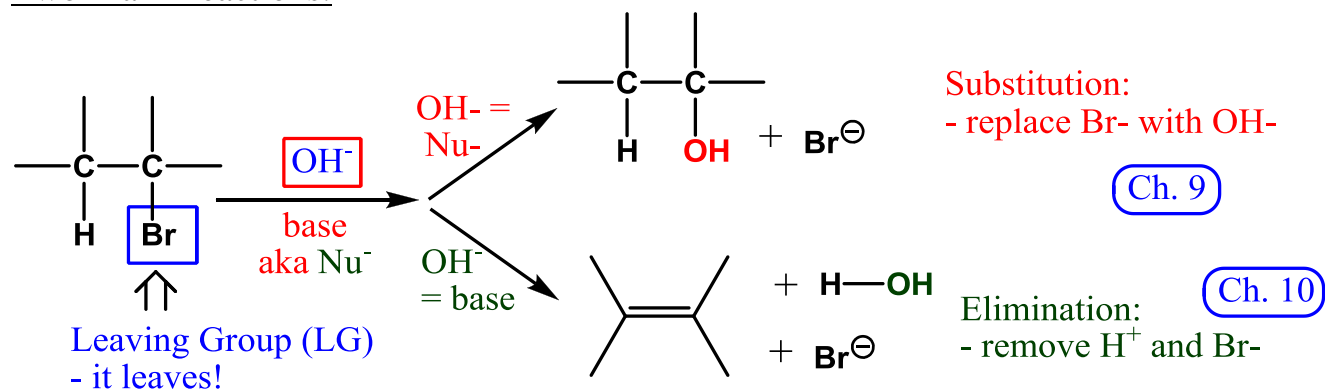
$\left. \begin{array}{l} \text{H-Cl} \\ \text{H-I} \end{array} \right\}$  one step of propagation is endothermic ∴ doesn't go  
 H-F - too exothermic

Now know 3 ways to make R-Br (or R-Cl etc.)

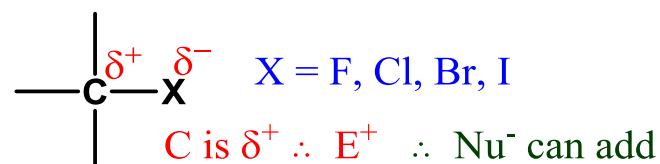
- 1)  $\text{R-H} + \text{Br}_2/h\nu$  or  $\text{Cl}_2/h\nu$
- 2)  $\text{R}_2\text{C=CR}_2 + \text{H-Br}$  (or HCl, HI, HF) - Markov
- 3)  $\text{R}_2\text{C=CR}_2 + \text{H-Br}/\text{H}_2\text{O}_2/h\nu$  - Anti-Markov

⇒ Can use these alkyl halides to make all kinds of other groups ⇒ next 2 chapters

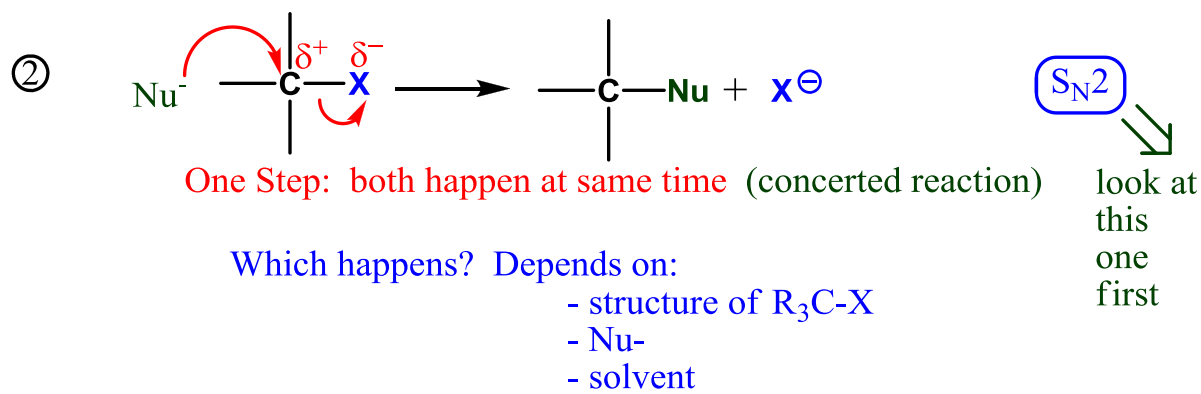
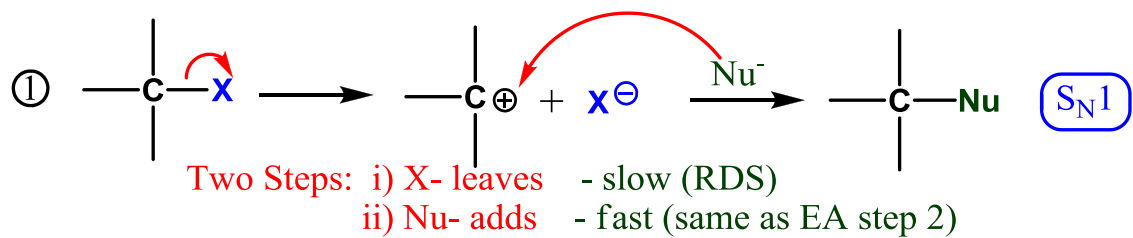
Two Main Reactions:



Nucleophilic Substitution Reactions



Two Possible Mechanisms: replace X- with Nu-



### S<sub>N</sub>2 Reaction

S: substitution

N: nucleophilic

2: bimolecular  $\Rightarrow$  2 molecules in RDStep  
(S<sub>N</sub>1 = unimolecular)