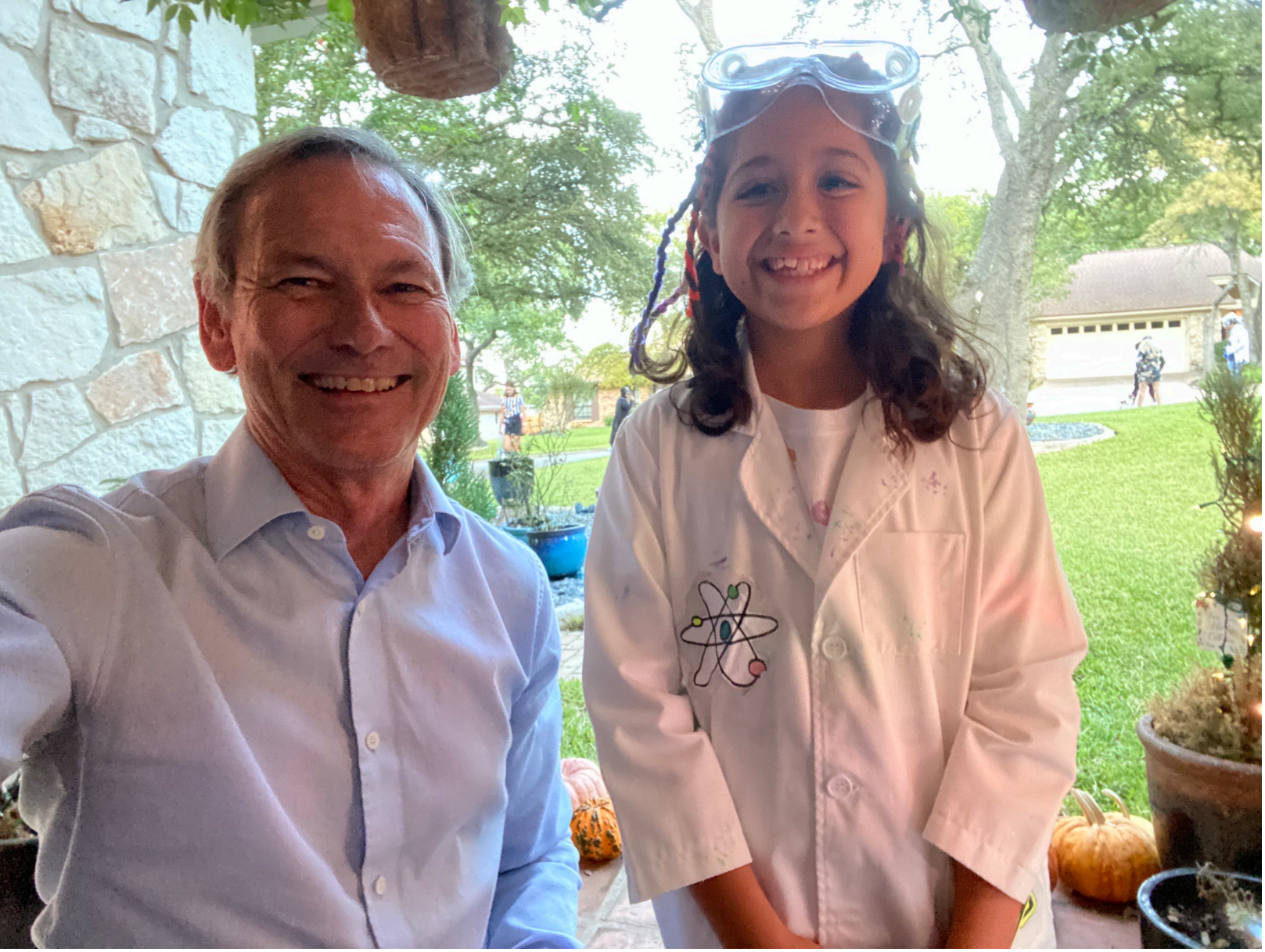

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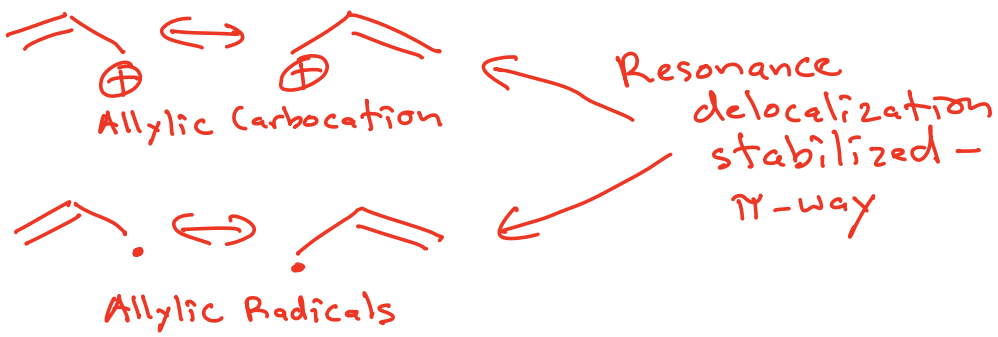
Allylic Halogenation

2 New Ideas

A)

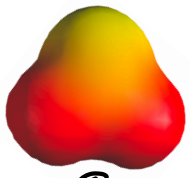


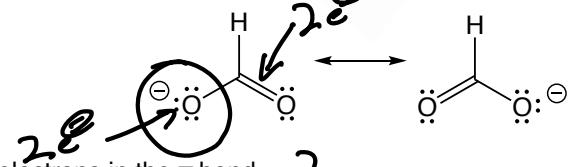
⟹ Radicals easily form on the carbons adjacent to a pi bond (C=C)

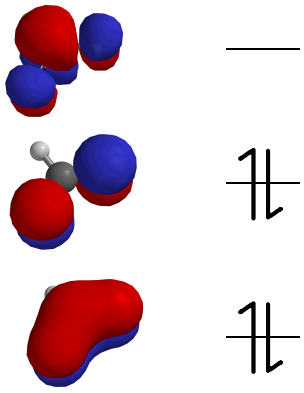
B) When given a choice in allylic halogenation reactions you always make the most stable alkene product

How to think about allyl radicals and allyl cations

Carboxylate anion





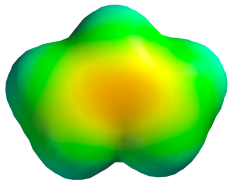


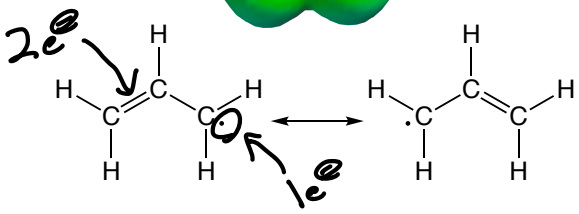
Total # of electrons in the π bond = 2

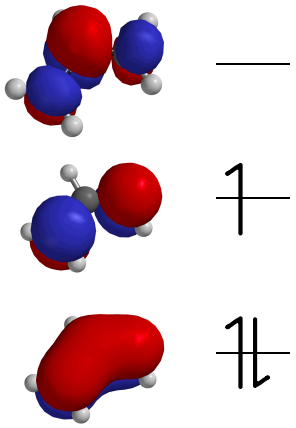
Total # of electrons in the 2p orbital of the other O atom = 2

Total # of electrons in the π-way = 4

Allyl radical





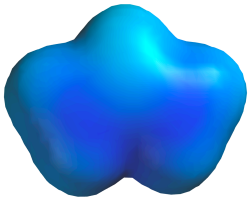


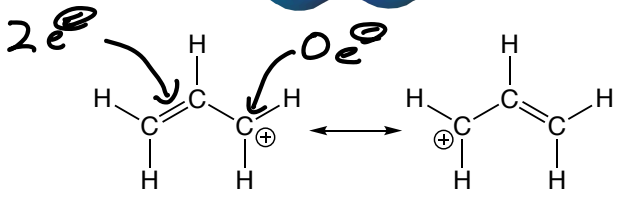
Total # of electrons in the π bond = 2

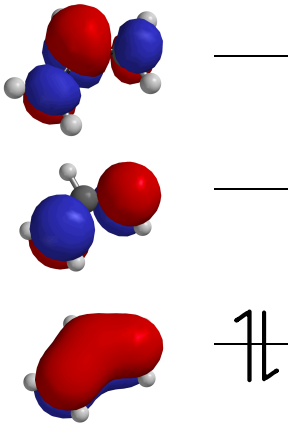
Total # of electrons in the 2p orbital of the other C atom = 1

Total # of electrons in the π-way = 3

Allyl cation







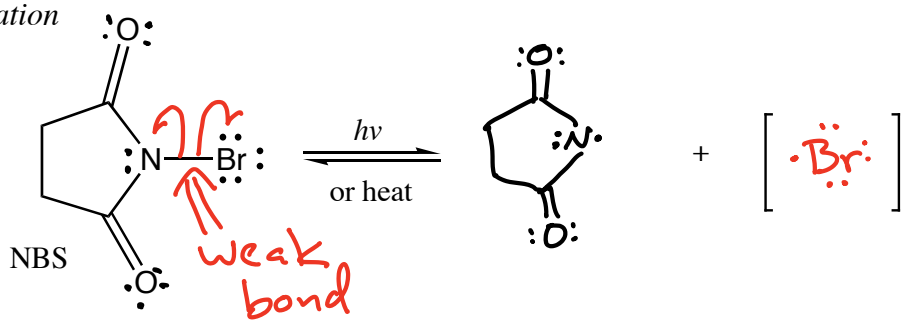
Total # of electrons in the π bond = 2

Total # of electrons in the 2p orbital of the other C atom = 0

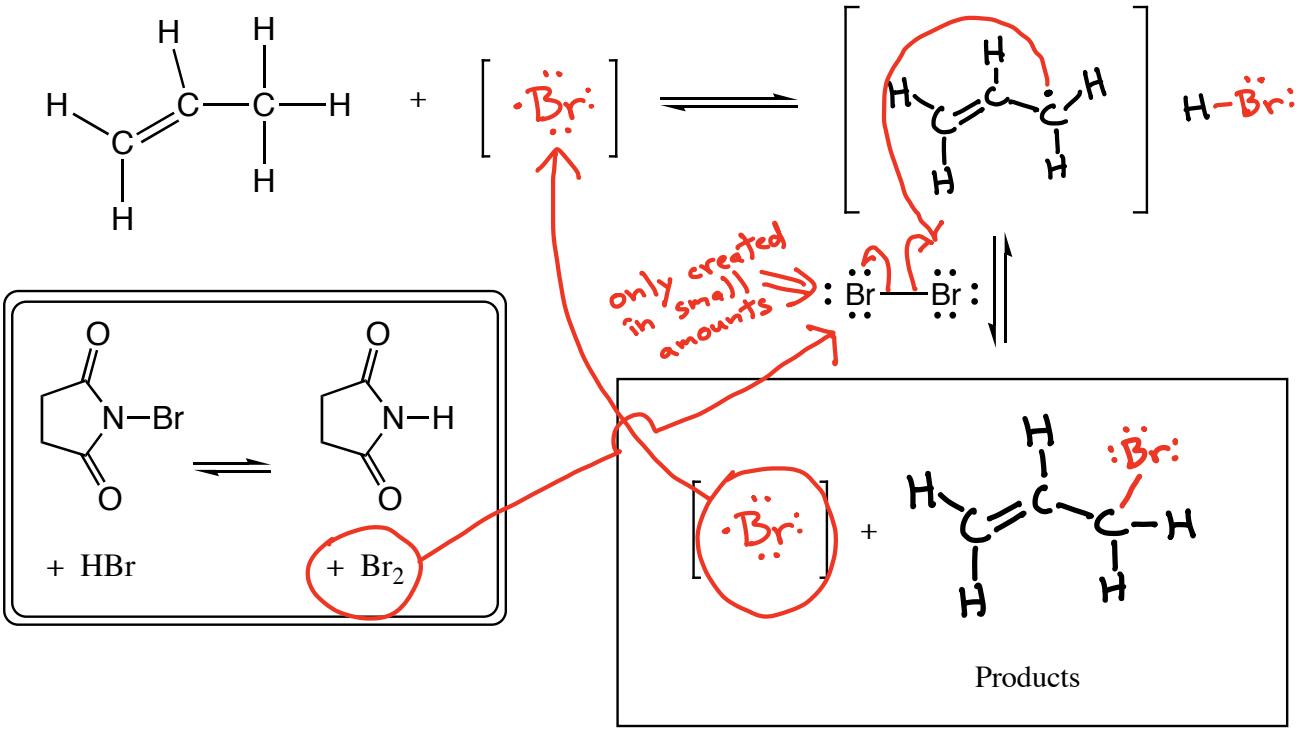
Total # of electrons in the π-way = 2

Allylic Halogenation

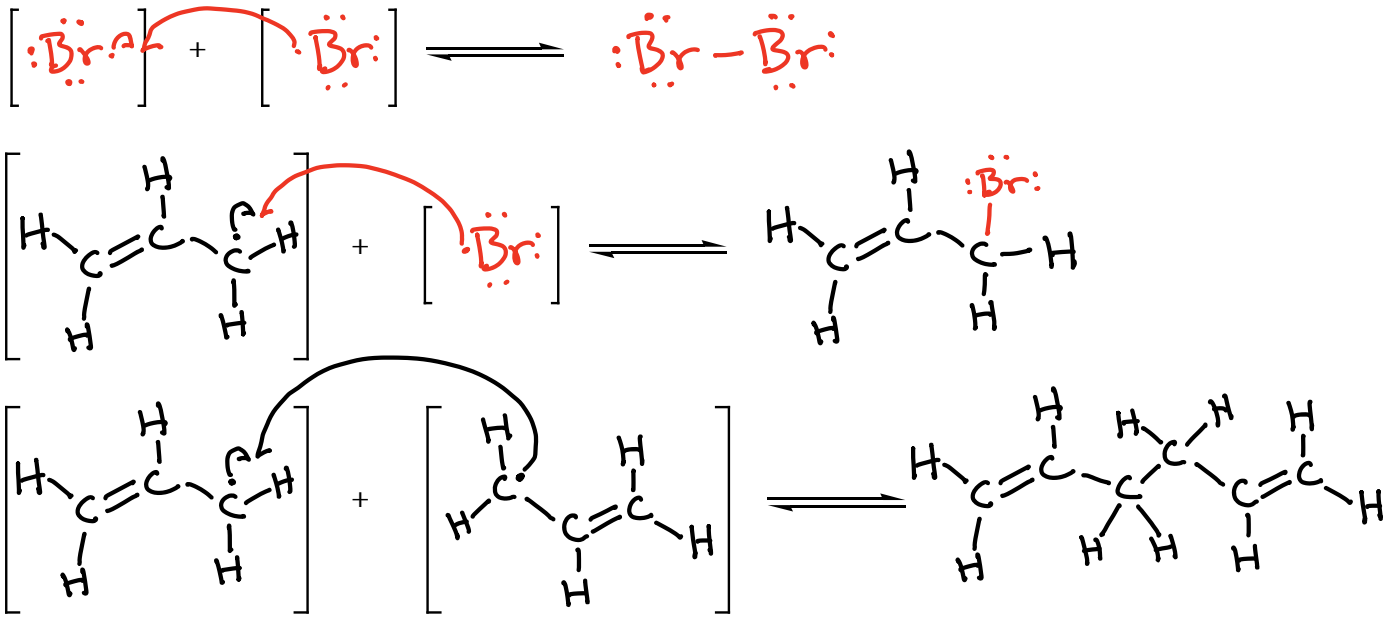
Initiation



Propagation

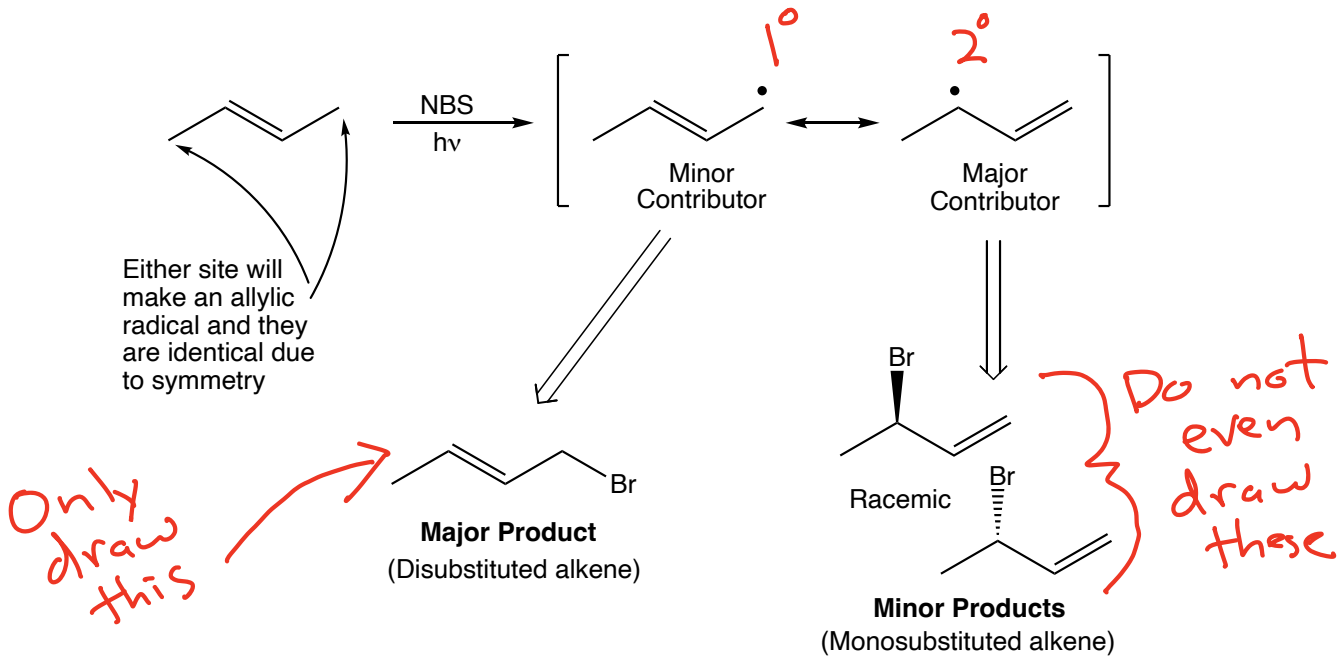


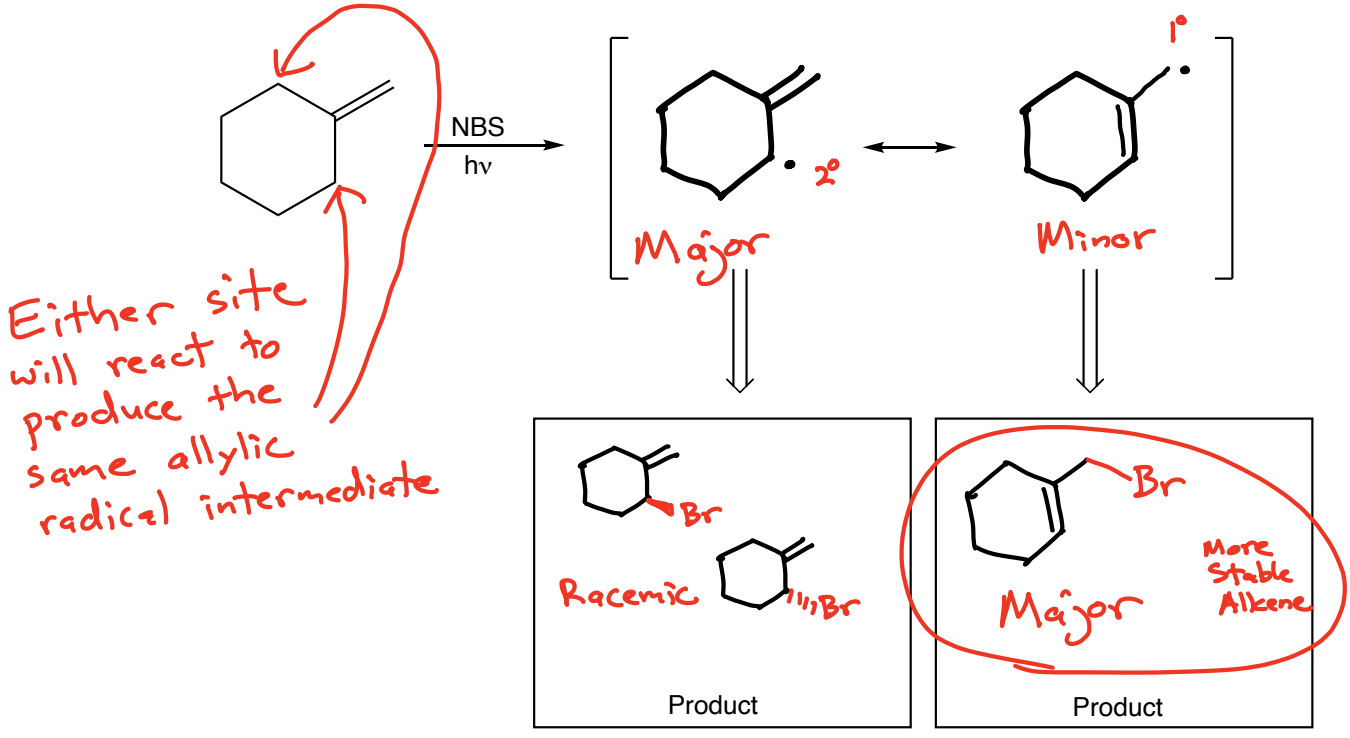
Termination



When analyzing allylic halogenation reactions (NBS and hν)

1. **Consider <u>all</u> possible allylic radicals that can be formed.**
2. **Analyze <u>all</u> contributing structures for <u>all</u> of the allylic radicals.**
3. **Add a Br atom at the site of the unpaired electron for <u>all</u> contributing structures for <u>all</u> of the allylic radicals.**
4. **From <u>all</u> of the possible products, the predominant product is the one THAT IS THE MOST STABLE ALKENE – the most substitued alkene – alkyl groups stabilize alkenes – *trans* over *cis*.**
5. **Note: It is OK if the product you choose derives from an allylic radical contributing structure that is a minor contributor. FOR THIS REACTION WE ONLY CARE ABOUT THE RELATIVE STABILITIES OF THE PRODUCT ALKENES.**

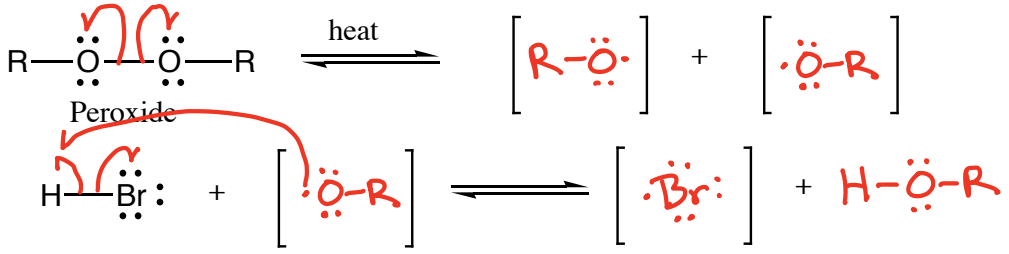




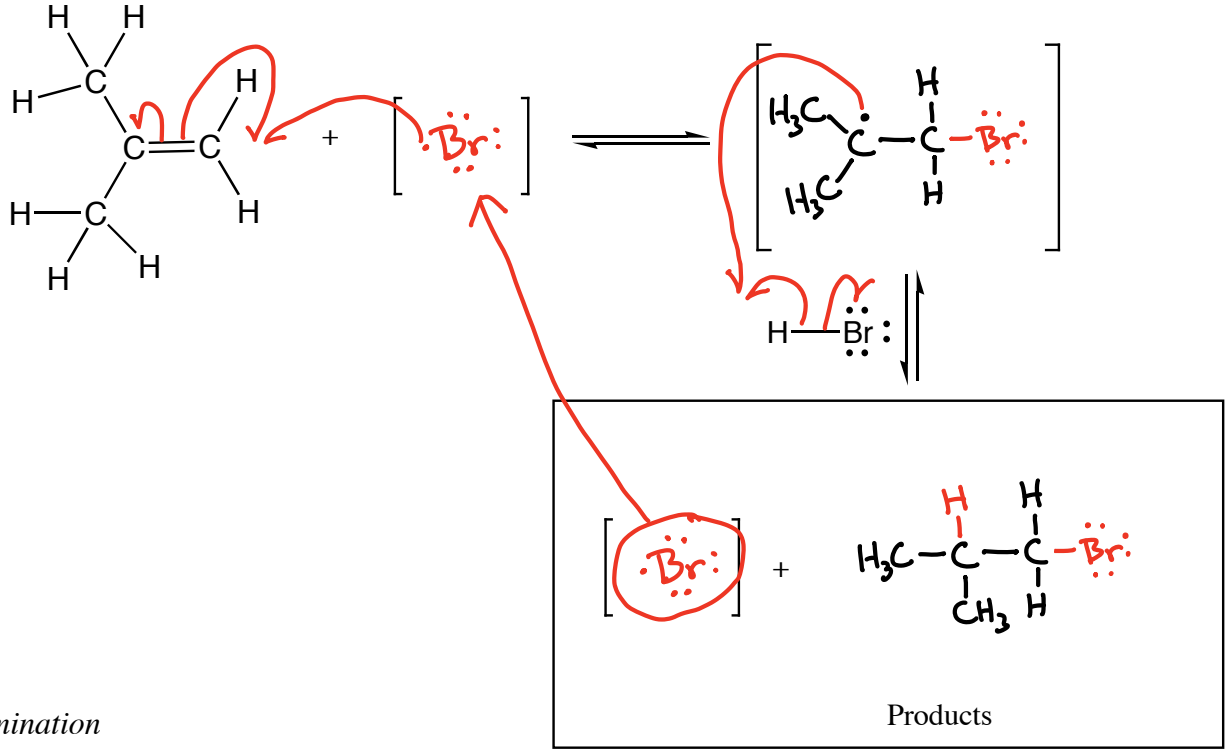
Big Change — For this reaction you need to choose the most stable product, NOT worrying about the most stable contributing structure of an allylic radical intermediate.

Non-Markovnikov Addition of HBr to an Alkene

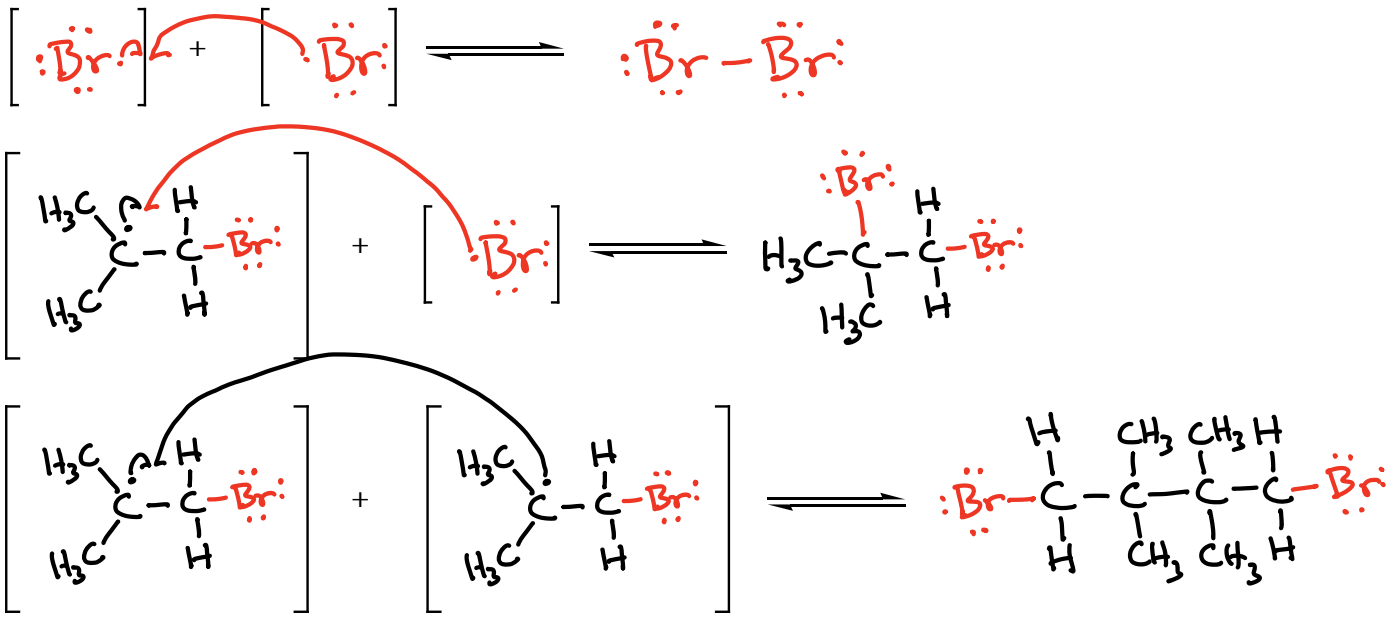
Initiation



Propagation



Termination



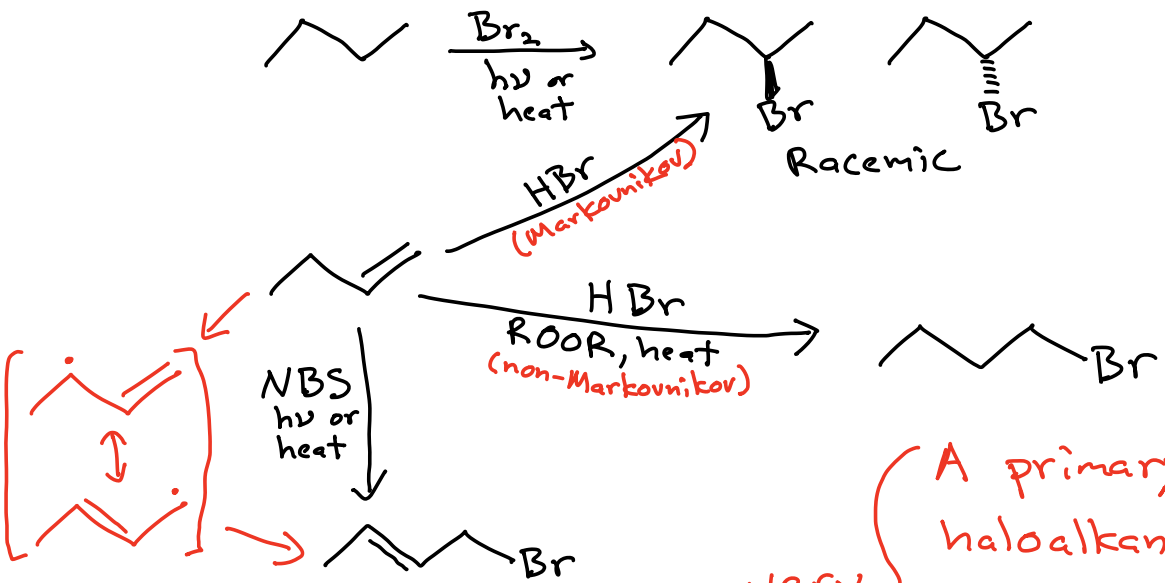
For subtle reasons (not discussed) H-Br, ROOR and heat gives very little allylic halogenation, and NBS/hν or heat gives very little alkene addition even though they both involve $[\cdot\ddot{\underset{\cdot\cdot}{Br}}:]$ and an alkene starting material.

Please accept this

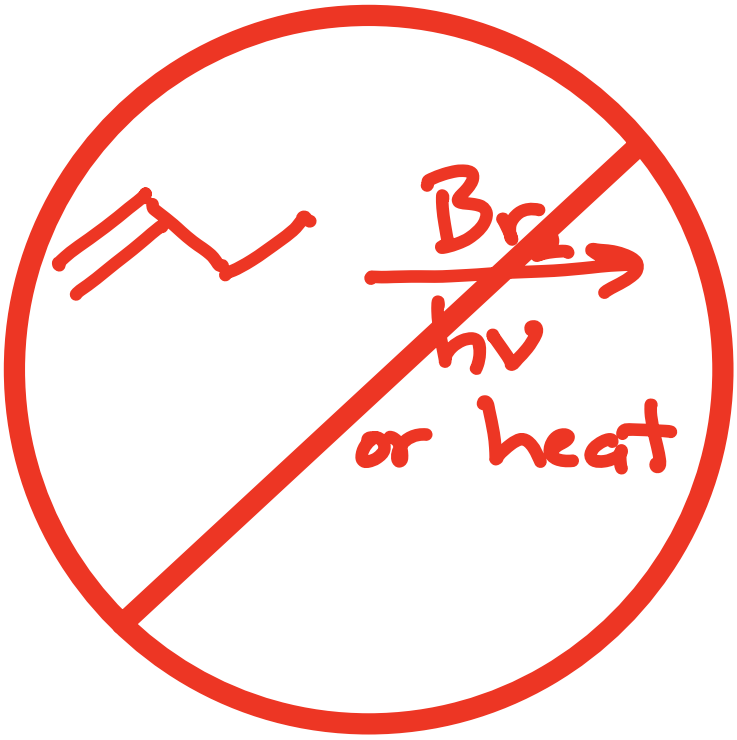
This is huge ↘

HBr
ROOR
heat
→ Non-Markovnikov Regiochemistry

Making Haloalkanes



very useful } A primary (1°) haloalkane product from a terminal alkene



Never use Br_2 and hv or heat with an alkene!

New Concept → Leaving Group

A group that can make a single bond to carbon that can make a stable species when it departs

nucleophiles/bases

Halogens

$I > Br > Cl > F$

Not much of a leaving group

Leaving Group Ability

Anion Stability

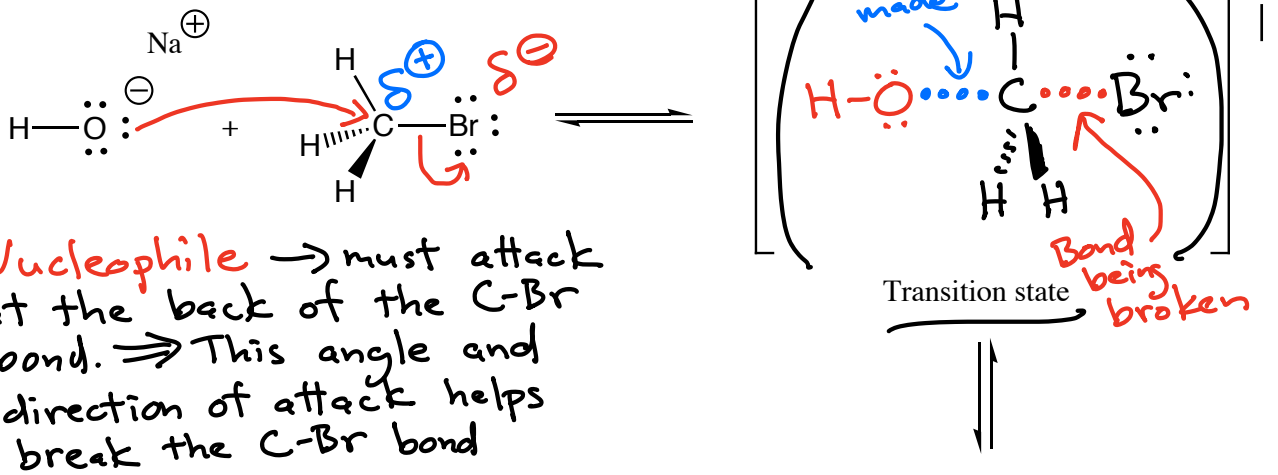
1st New Mechanism

S_N2 ← Bimolecular → both the haloalkane and nucleophile are involved in the rate-determining (slow) step of the reaction

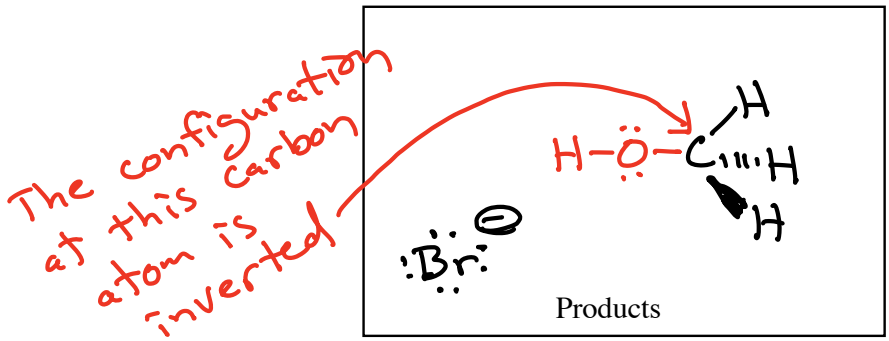
Substitution

Nucleophilic

The S_N2 Mechanism

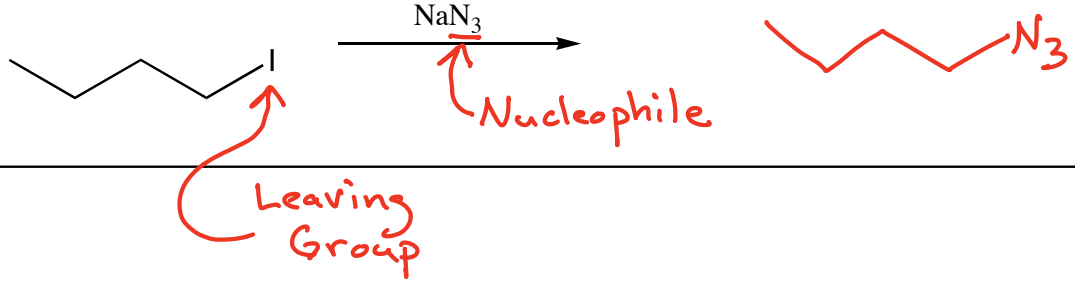


Nucleophile → must attack at the back of the C-Br bond. ⇒ This angle and direction of attack helps break the C-Br bond



Summary: The nucleophile attacks by making a new bond to C from the back of the C-X bond just as X leaves

Regiochemistry: N/A

Stereochemistry: INVERSION at the site of reaction

Example: