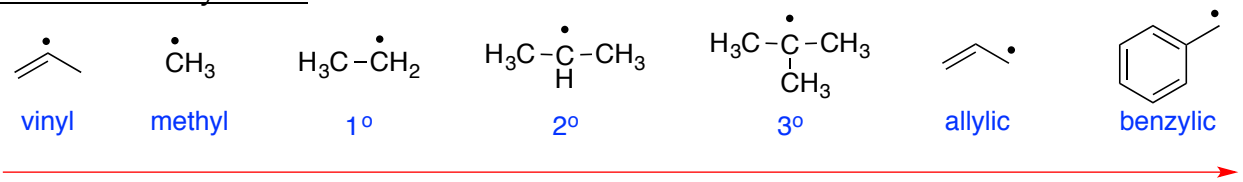
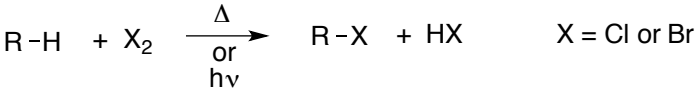
Chapter 10 Reaction Summary
Radical Reactions

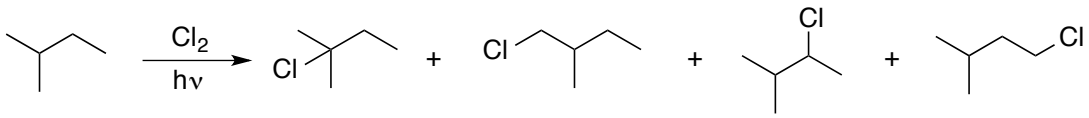
Radical Stability Trend



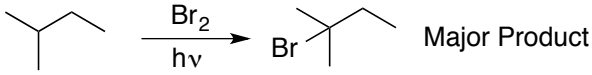
Radical Halogenation



- Radical halogenation can be initiated by heat or light.
- Cl_2 and Br_2 can be used. F_2 is too reactive while radical iodination is endothermic.
- Radical chlorination is not selective and there is the potential to get a chlorine at every carbon that containing a hydrogen.

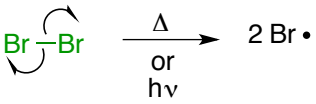


- Radical bromination is much more selective. The major product from a bromination will be the one that results from the most stable radical intermediate. 3°>2°>1°>methyl.

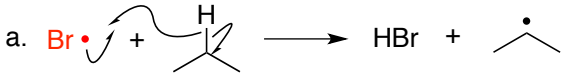


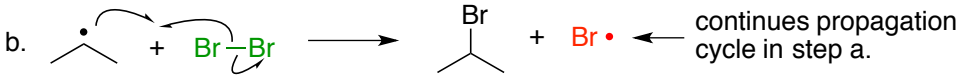
- Radical chain mechanisms have three steps: 1. Initiation, 2: propagation, 3: termination.

Initiation

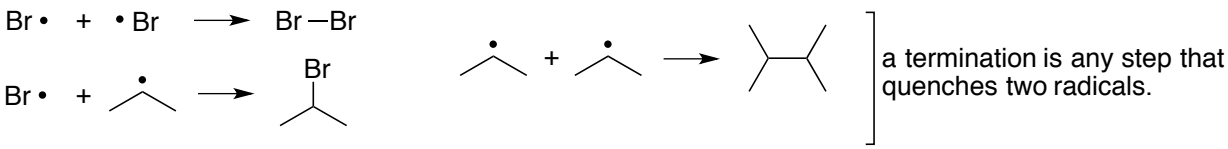


Propagation





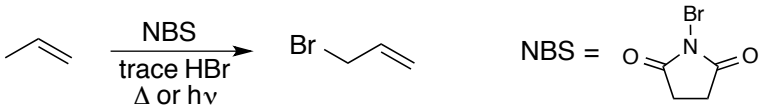
Termination



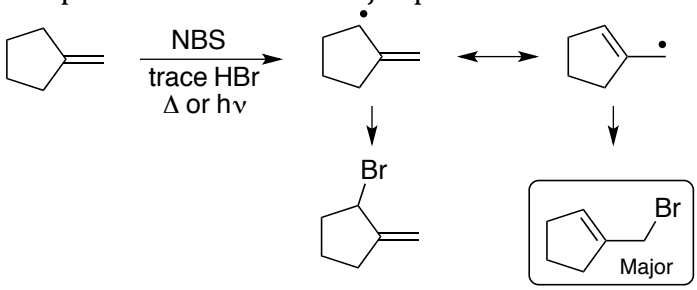
Common Mistake – An extremely common misstate is to confuse the propagation step in the mechanism with the termination step. Although one of the termination steps does produce a molecule of the desired product, this termination does not happen often and does not produce a significant amount of product. The propagation cycle is where significant product formation occurs.

Allylic Bromination

- The allylic position of an alkene can be brominated using NBS in the presence of trace hydrobromic acid and an initiator such as heat or light.

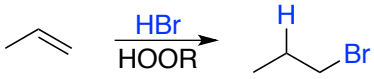


- Allylic radicals have 2 or more resonance structures. The bromination product can result from each resonance structure. If one product has a more highly substituted double bond, that product will be the major product.



- NBS provides a very low equilibrium concentration of Br_2, which is the active brominating agent.

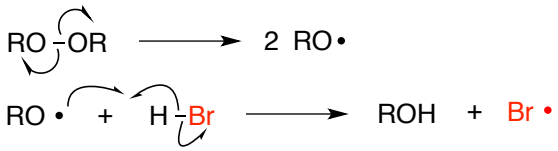
Radical Addition of HBr to Alkenes



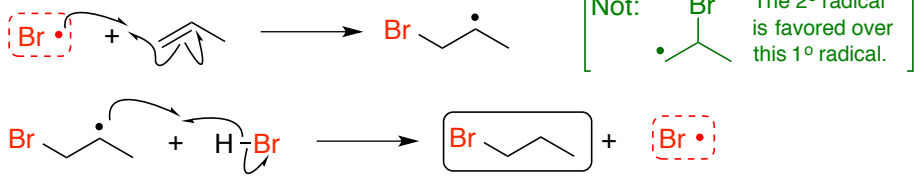
Anti-Markovnikov addition - H goes to the more substituted carbon and Br goes to the less substituted carbon.

- Addition of HBr to an alkene in the presence of peroxides changes the reaction from an ionic mechanism to a radical mechanism.
- By changing the mechanism, the regioselectivity of the reaction is changed. In the presence of peroxides, HBr is added in an anti-Markovnikov fashion.
- The peroxide acts as a radical initiator. The O-O bond is so weak that it undergoes homolysis to give a peroxy radical which initiates the radical process.
- Three step mechanism: 1. Initiation, 2: propagation, 3: termination.

Initiation



Propagation



Termination

-any step where two of the radicals from above come together