

## Organic Chemistry 1 Resource- week 13

Hi everyone! This week most classes are working on chapter 11. This chapter is very different from the others you've learned so far, so make some time to really sit down and digest some of this. Happy studying! **Don't forget that group tutoring is Tuesday at 5:30 Here is the link.**

[https://www.baylor.edu/support\\_programs/index.php?id=40917](https://www.baylor.edu/support_programs/index.php?id=40917)

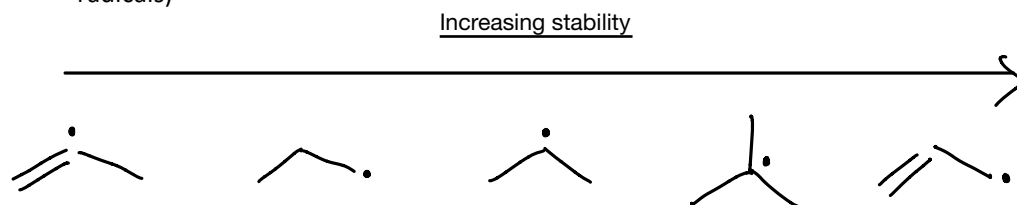
**Key Words:** Radicals, radical stability, radical mechanism steps, radical halogenation, allylic bromination

### Introduction to radicals

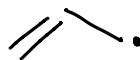
- What is a radical?
  - A radical is an unpaired valence electron
- Two ways to split a bond:
  - **Heterolytic cleavage**- both electrons of bond goes one way and forms ions
  - **Homolytic cleavage**- the electrons of the bond go opposite ways forming radicals



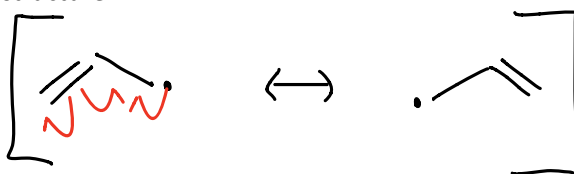
- Radical Stability
  - Tertiary radicals are most stable (like carbocations)
  - However, radicals that participate in resonance are even more stable than tertiary (allylic radicals)



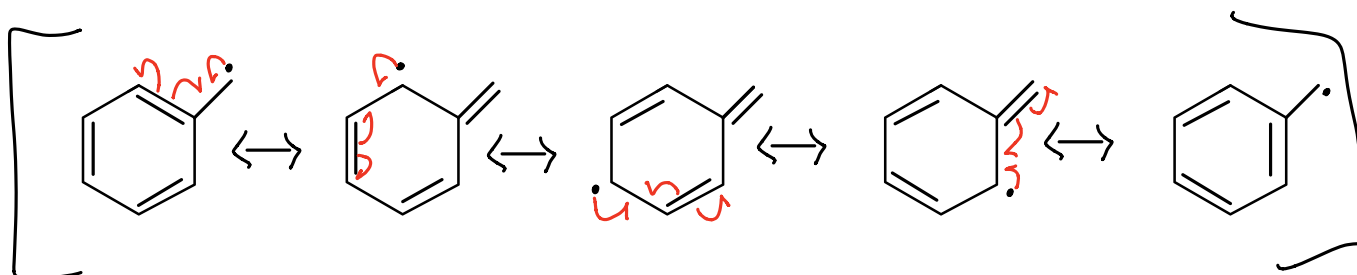
- Resonance structures of radicals
  - This is the basic resonance pattern for radicals: an unpaired electron in the allylic position to a pi bond



- This unpaired electron is resonance stabilized, and three arrows can be used to draw the resonance structure



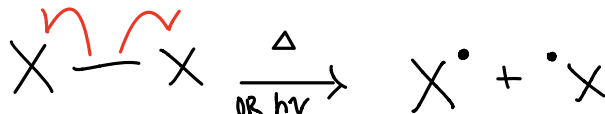
- Benzylic positions also exhibit this pattern



## Common patterns of radical mechanisms

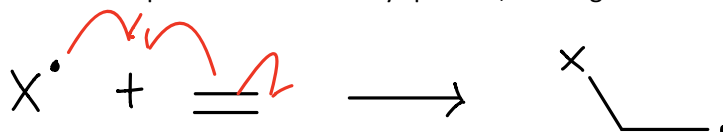
### 1. Homolytic cleavage:

- This requires a large input of energy from either heat or light



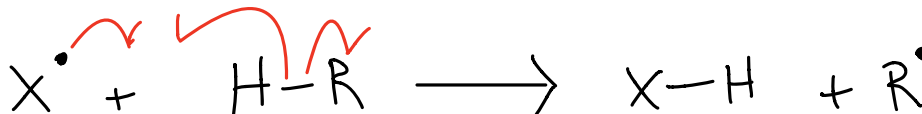
### 2. Addition to a pi bond

- A radical adds to a pi bond and it destroys pi bond, forming new radical



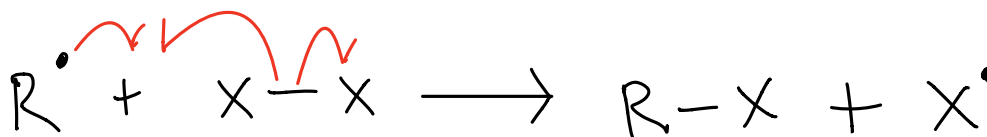
### 3. Hydrogen abstraction

- Radicals can abstract a hydrogen
- This is NOT a proton transfer. A proton transfer can only be in ionic steps
  - i. A proton transfer involves the movement of the nucleus of the hydrogen leaving behind the electron. In a hydrogen abstraction, the entire hydrogen atom including the electron is moved.



### 4. Halogen abstraction

- A radical can abstract a halogen and generate a new radical



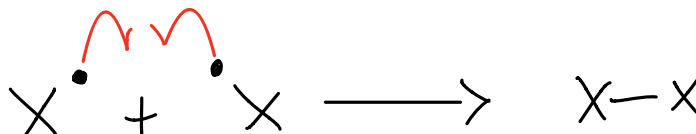
### 5. Elimination

- This is the opposite of addition to a pi bond.

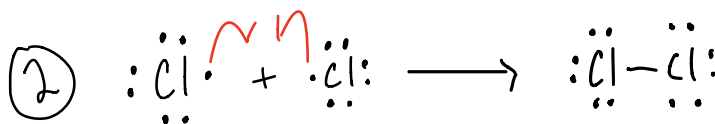
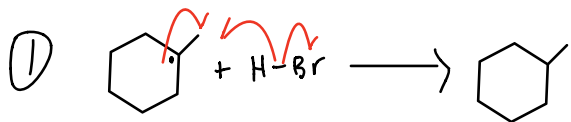


### 6. Coupling

- This is the opposite of homolytic cleavage

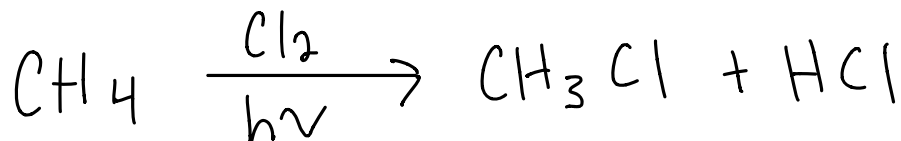


Practice: Identify the following mechanism steps



### Radical halogenation

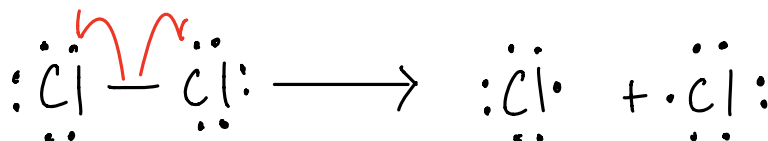
- Overall reaction



<https://www.khanacademy.org/science/organic-chemistry/substitution-elimination-reactions/free-radical-reaction-alkanes/v/free-radical-reactions>

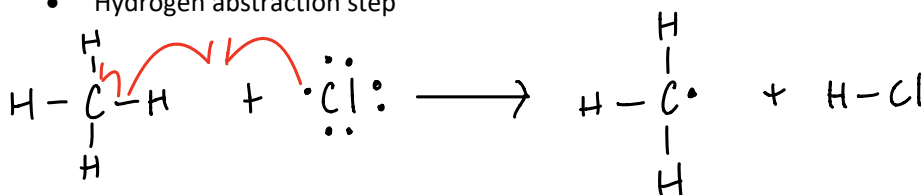
- This proceeds via a radical mechanism with 3 main stages
  - Initiation- creation of radicals
  - Propagation- hydrogen abstraction and halogen abstraction
  - Termination- termination of the radicals

#### 1. Initiation- homolytic cleavage

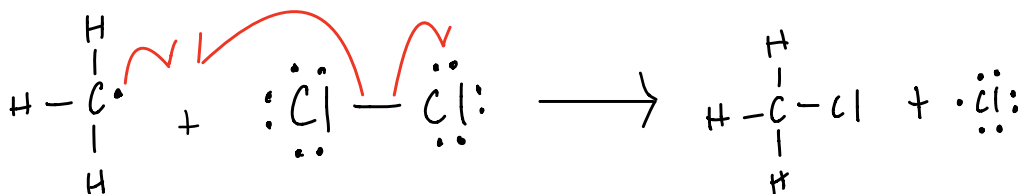


#### 2. Propagation

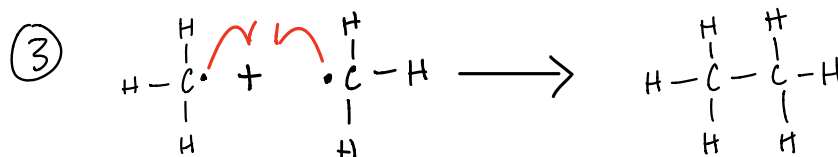
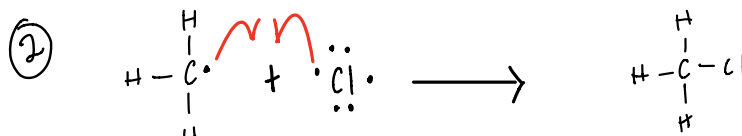
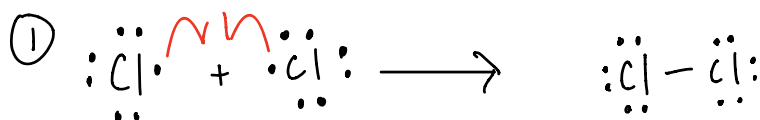
- Hydrogen abstraction step



- Halogen abstraction step

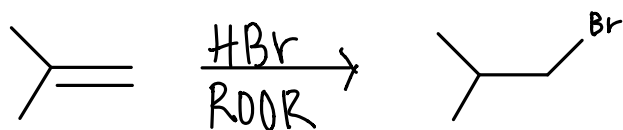


#### 3. Termination- 3 coupling steps



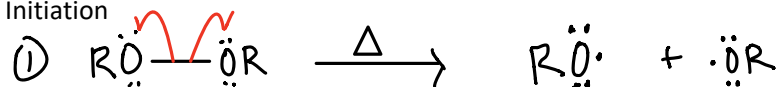
### Radical addition of HBr: anti-markovnikov addition

- Remember that addition of HBr across a double bond in the presence of peroxides will cause the addition to occur anti-mark

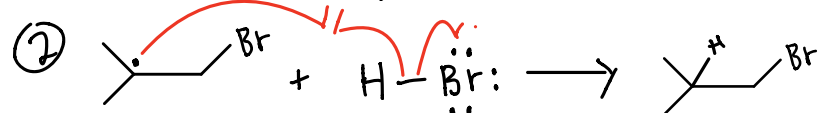
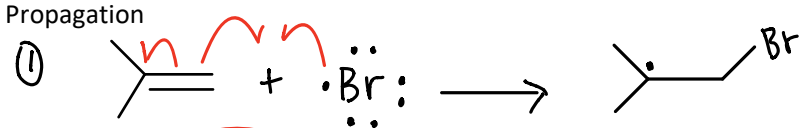


- Anti-mark mechanism for addition of HBr

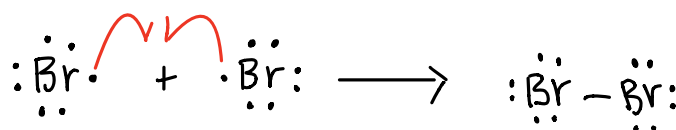
#### 1. Initiation



#### 2. Propagation



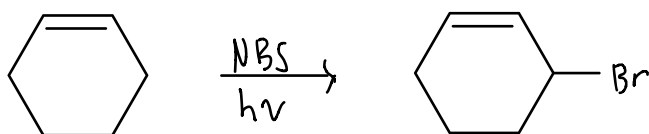
#### 3. Termination



This step puts the radical in the most stable position, which is more substituted

### Allylic Bromination- Bromination of Alkenes

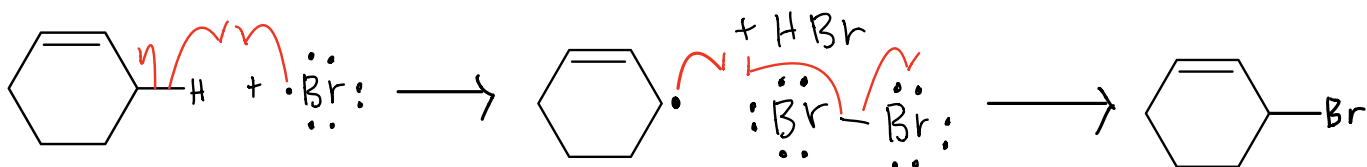
- Bromination of alkenes will take place at the allylic position



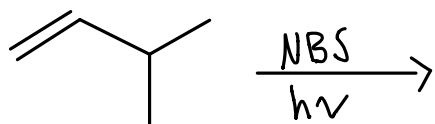
[https://www.youtube.com/watch?v=BV\\_9wkYTeyA](https://www.youtube.com/watch?v=BV_9wkYTeyA)

- Using this reagent however will cause competition between radical halogenation and ionic addition of Br<sub>2</sub>
  - So instead of Br<sub>2</sub>, we use **NBS** to select for only radical bromination

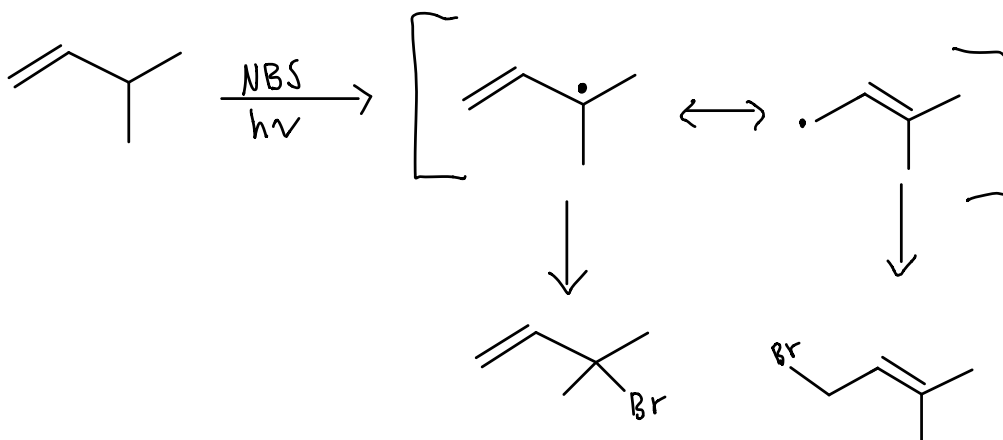
- Mechanism:



- In this mechanism, a radical is produced in allylic position on a nonsymmetric molecule



- Why is this important? It will produce 2 products!!



Answers to practice!

1. Hydrogen abstraction
2. Coupling