

# **Free Radical Reactions**

## **2 - Alkyl Halide Synthesis**

*Dr. Sapna Gupta*

# Alkyl Halide Synthesis - Introduction

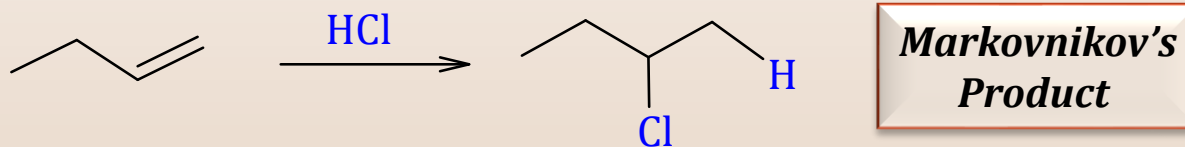
This power point is a summary of all the reactions you have learned of alkyl halide synthesis. Substitution and elimination reactions show us how important alkyl halides are in organic reactions.

Alkene, alkyne and free radical reactions give us a many ways of synthesizing exactly the substrate we might need for a reaction.

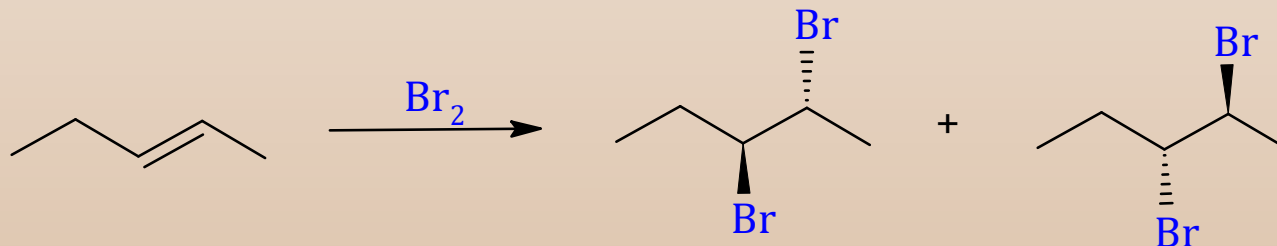
The following slides is a summary of all the reactions we have done so far to make alkyl halides.

# From Alkenes – Addition Reactions

- Hydrohalogenation of alkene (Markovnikov's addition)

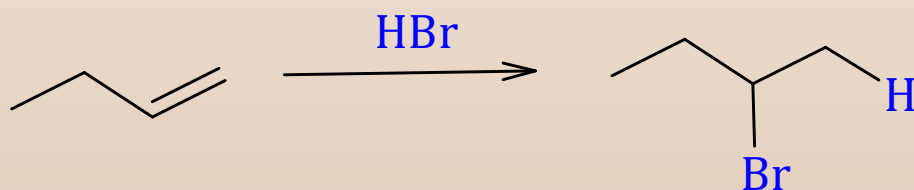


- Halogenation of alkenes (anti vicinal addition)

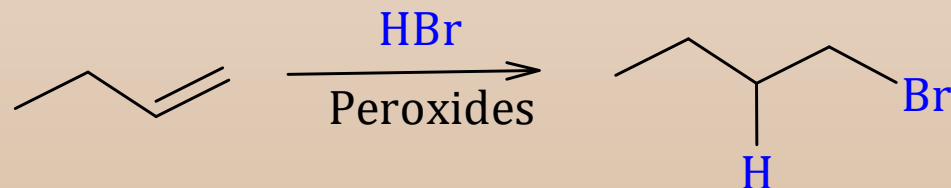


# From Alkenes - Radical Addition

- Addition of HBr to alkenes, in presence of energy (free radical reaction), gives anti-Markovnikov addition (*H goes to C with less H*).
  - Markovnikov addition occurs when radicals are absent.
  - Anti-Markovnikov addition occurs when peroxides or other sources of radicals are present.
- **Note:** Addition of HCl and HI is only Markovnikov's addition.



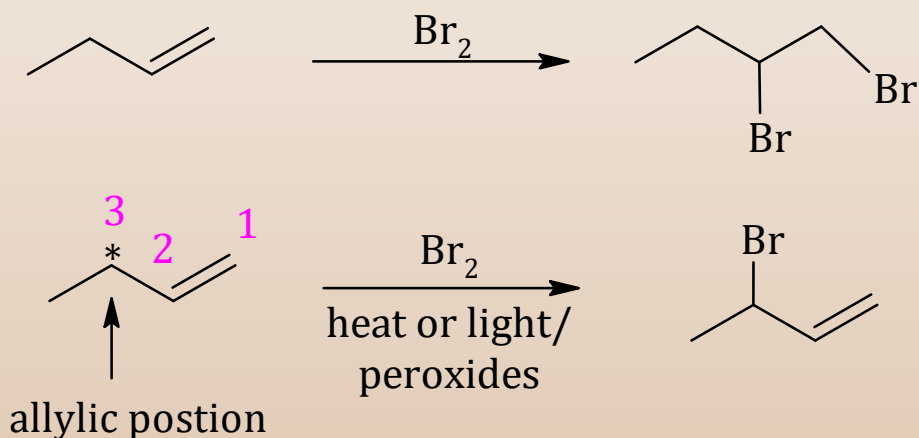
**Markovnikov's  
Product**



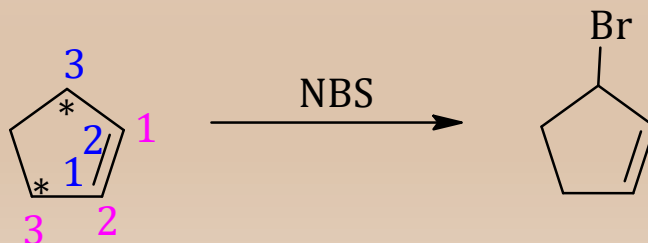
**Anti-Markovnikov's  
Product**

# From Alkenes - Radical Allylic Substitution

- Alkenes undergo allylic substitution on addition of  $\text{Br}_2$ , in presence of energy (free radical mechanism). (*Allylic position is the 3<sup>rd</sup> carbon from the start of the double bond, in the structure below it is marked 3\**)

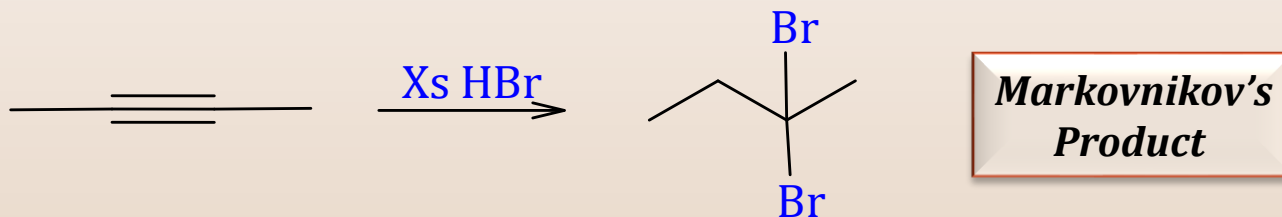


- This substitution can be achieved by using N-bromosuccinimide (NBS). It works also via free radical mechanism. (*The \* carbons are the allylic positions.*)

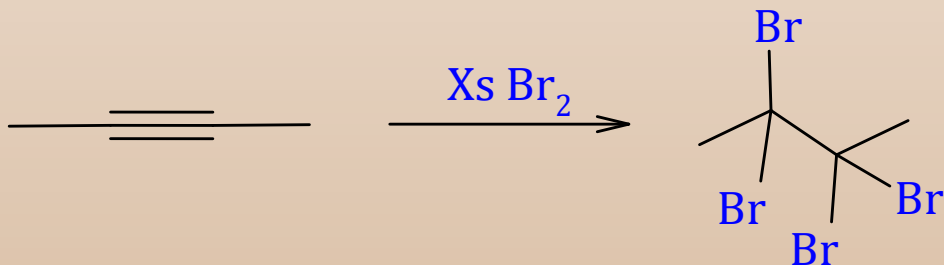


# From Alkynes – Addition Reactions

- Hydrohalogenation of alkynes (Markovnikov's addition giving geminal halides),



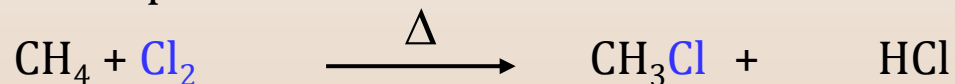
- Halogenation of alkynes



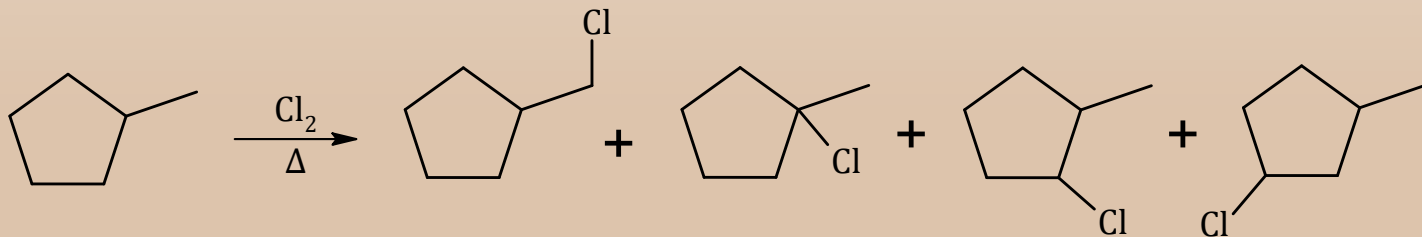
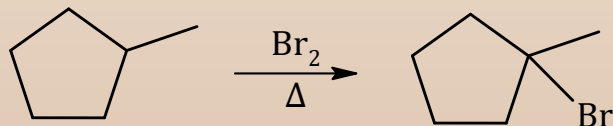
# From Alkanes – Free Radical

Alkanes can be halogenated by substitution reaction via free radical mechanism only.

- It requires heat or some energy to get started in addition to an initiator e.g., bromine or peroxides.

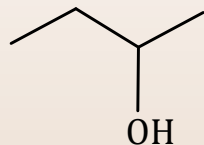


- Major product formed in case of bromination is the one from the most stable radical. Chlorination is not specific as it is very reactive.

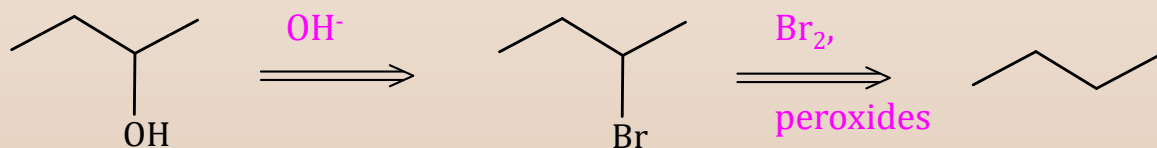


## Solved Problem: Solving for synthesis

Show how you will carry out the following synthesis from an alkane, using what you have learned so far in substitution, elimination, alkene, alkyne and free radical reactions.



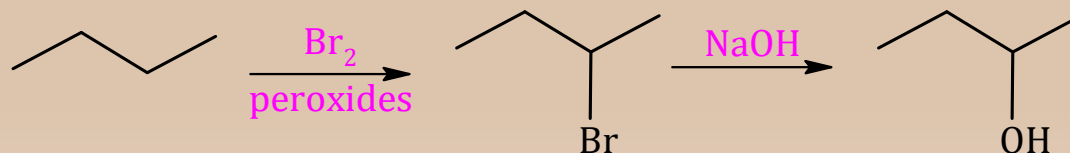
**ANSWER:** I have solved this as retrosynthesis so you get used to going in reverse.



OH group can be obtained by substitution reaction of a LG. A LG, Br, can be made on an alkane only by free radical reaction.

You can also use light energy,  $h\nu$ , or heat,  $\Delta$  for the free radical conditions to indicate that it is a free radical reaction.

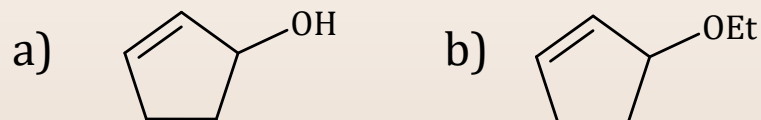
If writing as a forward reaction it will be the same but in reverse.



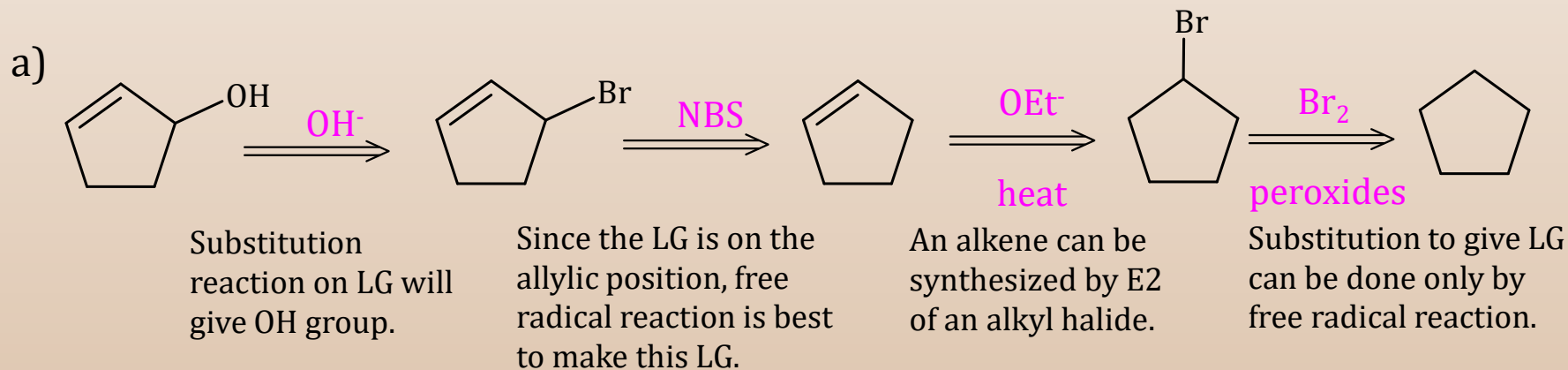


## Solved Problem: Solving for synthesis

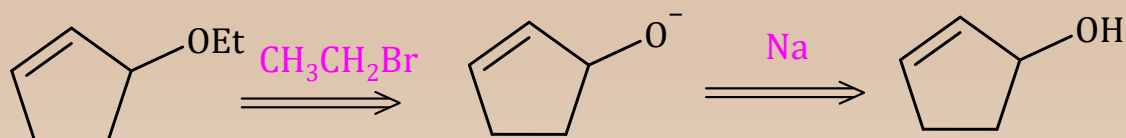
Show how you will carry out the following synthesis from an alkane, using what you have learned so far in substitution, elimination, alkene, alkyne and free radical reactions.



**ANSWER:** I have solved this as retrosynthesis so you get used to going in reverse.



b) This is a continuation of a). I could have asked only for b) but it would be a six step synthesis 😊. I will do retrosynthesis upto the alcohol in a), rest is the same as a).



# Key Concepts

- Synthesis of alkyl halides from
  - Alkenes
  - Alkynes
  - Alkanes