Free Radical Reactions
2 - Alkyl Halide Synthesis

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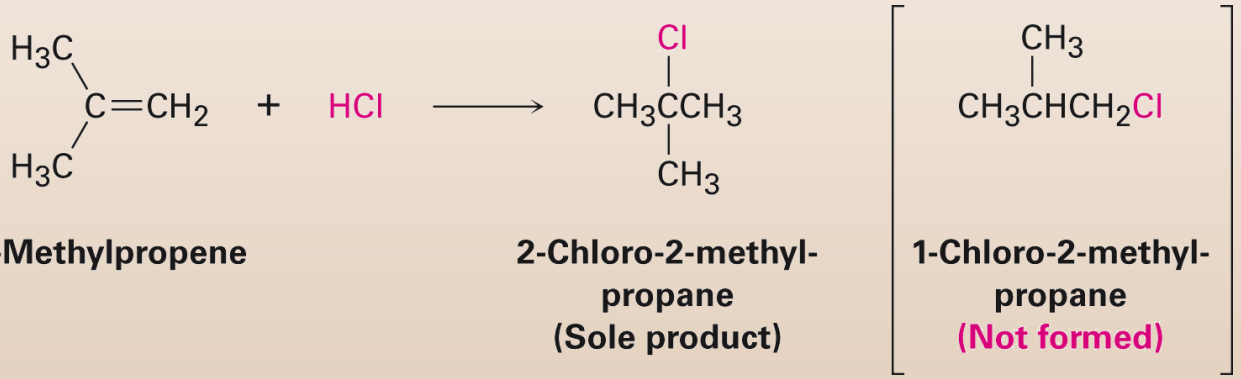
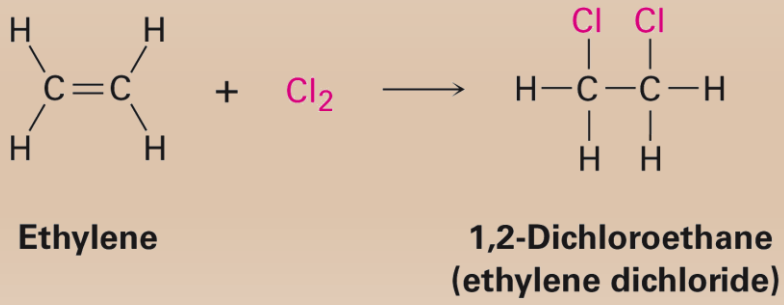
Synthesis – From Alkenes

- Hydrohalogenation of alkene (Markovnikov's addition)

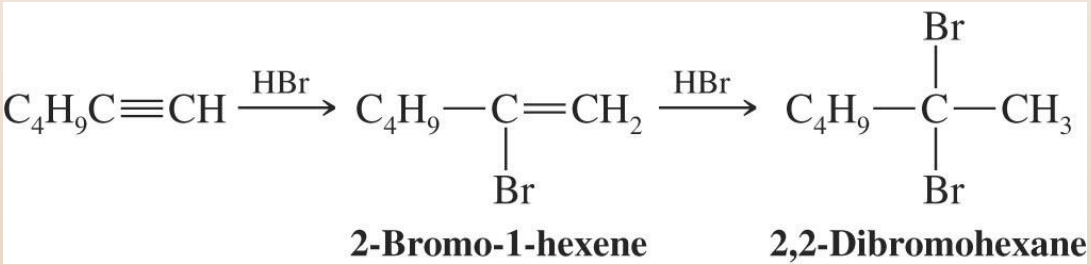


- Halogenation of alkenes (anti addition)



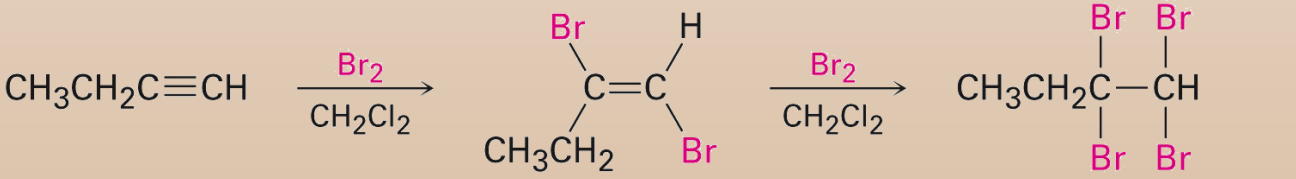
Synthesis – From Alkynes

- Hydrohalogenation of alkynes (Markovnikov's addition)



2-Bromo-1-hexene **2,2-Dibromohexane**

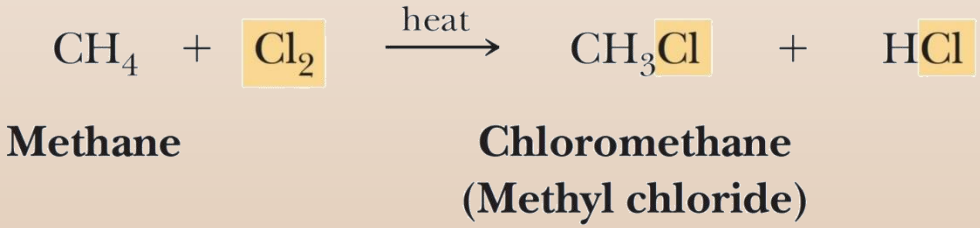
- Halogenation of alkynes



1-Butyne **(*E*)-1,2-Dibromo-1-butene** **1,1,2,2-Tetrabromobutane**

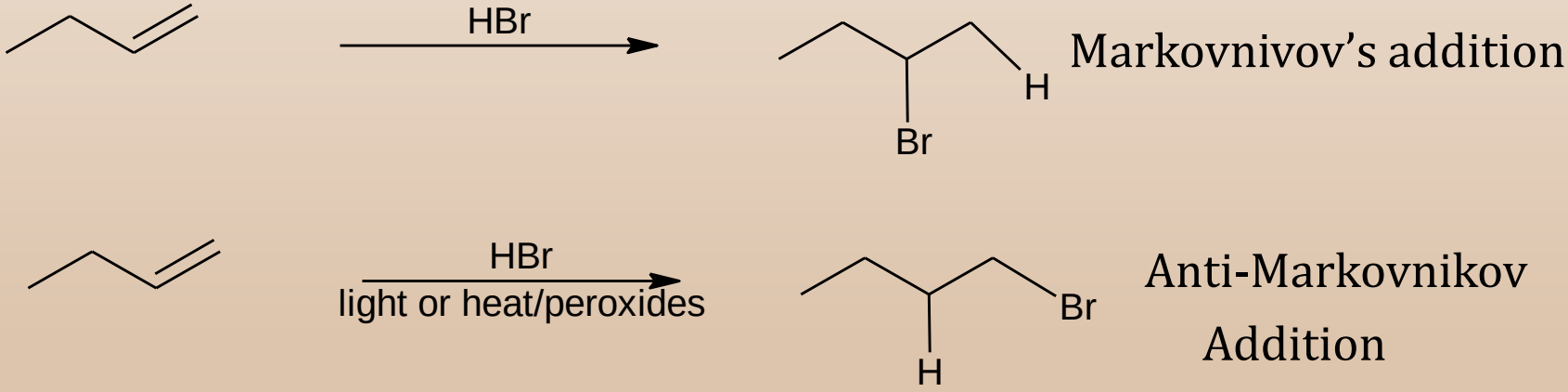
Synthesis – From Alkanes

- Alkanes can be halogenated by substitution reaction.
- The mechanism is free radical.
- It requires heat or some energy to get started



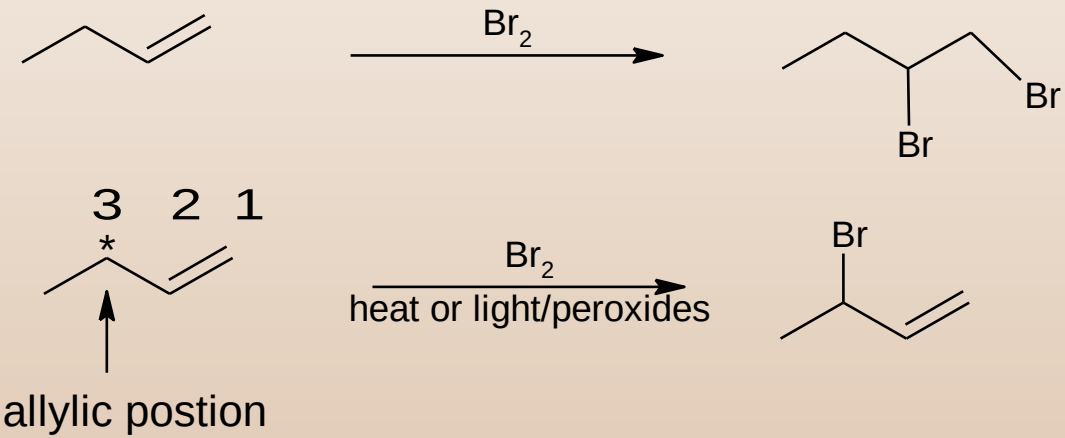
Radical Addition on Alkenes

- 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.

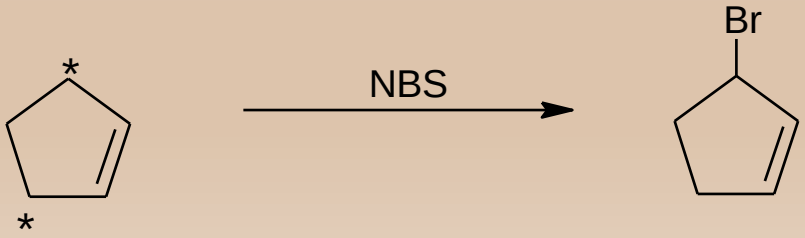


Radical Allylic Substitution on Alkenes

- Alkenes undergo allylic substation on addition of Br_2, in presence of energy (free radical mechanism). (*Allylic position is the 3rd 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 in the free radical mechanism. (*The * carbons are the allylic positions*.)



Key Concepts

- Synthesis of alkyl halides from
  - Alkenes
  - Alkynes
  - Alkanes
- Regioselectivity of bromine (NBS)
- Allyl radical and resonance