Haloalkanes

Chapter 8

Structure

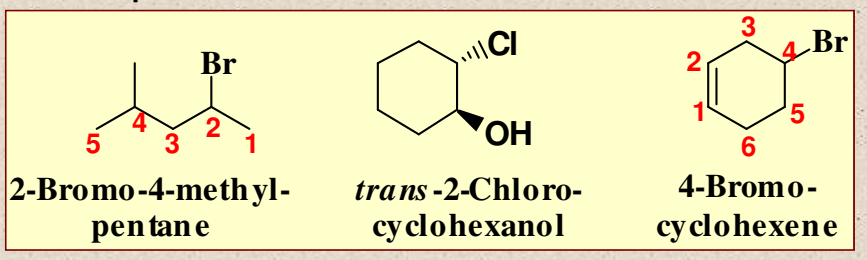
- Haloalkane (alkyl halide): A compound containing a halogen atom covalently bonded to an sp^3 hybridized carbon; given the symbol RX.
- Haloalkene (vinylic halide): A compound containing a halogen atom bonded to an sp^2 hybridized carbon.
- Haloarene (aryl halide): A compound containing a halogen atom bonded to a benzene ring; given the symbol ArX. We study these in Chapter 21.

Nomenclature

1. Number the parent chain to give the substituent encountered first the lowest number, whether it is halogen or an alkyl group.
2. Indicate halogen substituents by the prefixes fluoro-, chloro-, bromo-, and iodo- and list them in alphabetical order with other substituents.
3. Locate each halogen on the parent chain by giving it a number preceding the name of the halogen.
4. In haloalk**enes**, number the parent chain to give carbon atoms of the **double bond** the lower set of numbers.

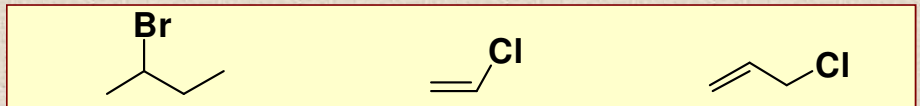
Nomenclature

– examples



2-Bromo-4-methyl-pentane | ***trans*-2-Chloro-cyclohexanol** | **4-Bromo-cyclohexene**

- Common names: name the alkyl group followed by the name of the halide.



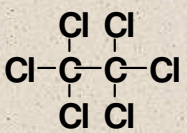
2-Bromobutane (*sec*-Butyl bromide) | **Chloroethene (Vinyl chloride)** | **3-Chloropropene (Allyl chloride)**

Nomenclature

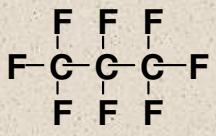
– Several polyhaloalkanes are common solvents and are generally referred to by their common or trivial names.

CH_2Cl_2	$CHCl_3$	CH_3CCl_3	$CCl_2=CHCl$
Dichloromethane (Methylene chloride)	Trichloromethane (Chloroform)	1,1,1-Trichloroethane (Methyl chloroform)	Trichloroethylene (Trichlor)

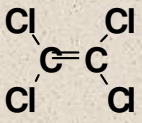
– Hydrocarbons in which all hydrogens are replaced by halogens are commonly named as perhaloalkanes or perhaloalkenes.



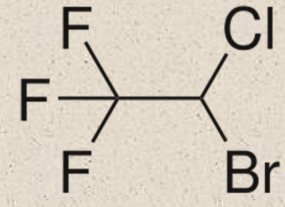
Perchloroethane



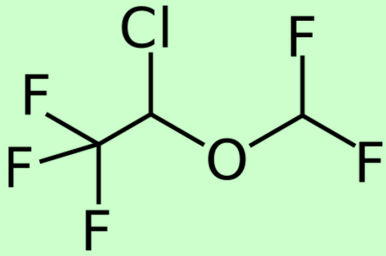
Perfluoropropane



Perchloroethylene



Halothane:
inhalational anesthetic (1950's)



Isoflurane: inhalational anesthetic

Discovered in 1963; not released for Use in the US until 1979

Van der Waals Forces

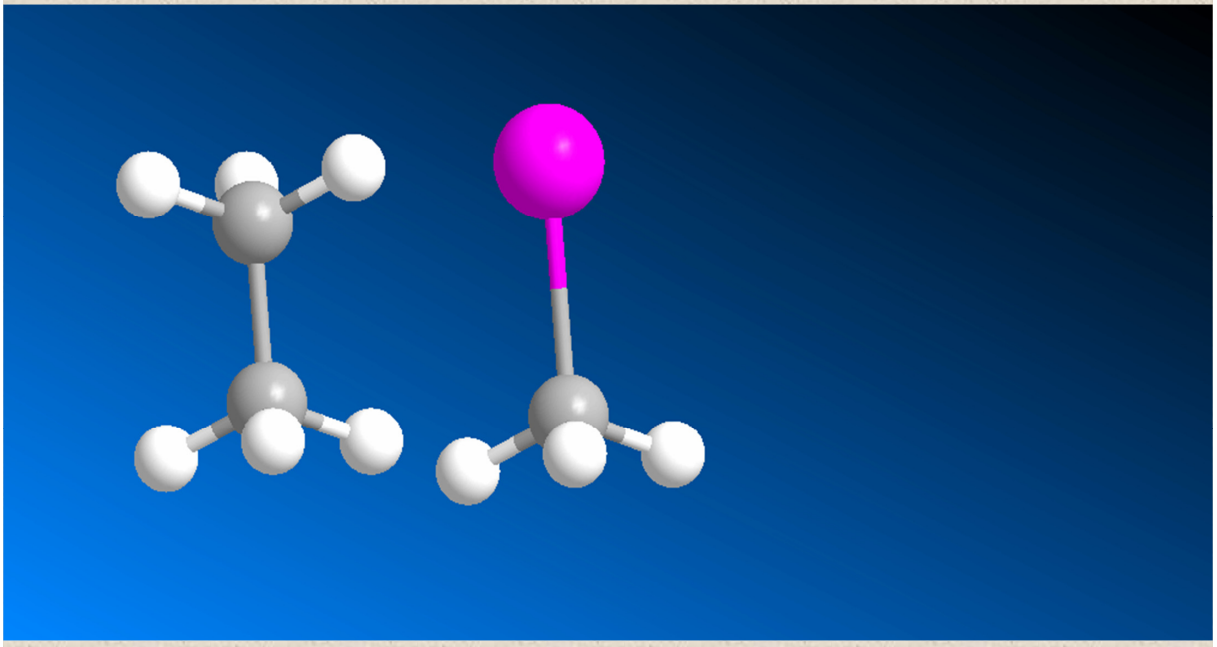
- Haloalkanes are associated in the liquid state by van der Waals forces.
- van der Waals forces: A group intermolecular attractive forces including:
  - dipole-dipole forces.
  - dipole-induced dipole forces.
  - induced dipole-induced dipole (dispersion) forces.
- van der Waals forces pull molecules together.
  - As molecules are brought closer and closer, van der Waals attractive forces are overcome by repulsive forces between electron clouds of adjacent atoms or molecules

Van der Waals Forces

- The energy minimum is where the attractive and repulsive forces are balanced.
- Nonbonded interatomic and intermolecular distances at these minima can be measured by x-ray crystallography and each atom and group of atoms can be assigned a van der Waals radius.
- Nonbonded atoms in a molecule cannot approach each other closer than the sum of their van der Waals radii without causing nonbonded interaction strain.

H	F	Cl	Br	CH_2	CH_3	I
120	135	180	195	200	200	215

Increasing van der Waals radius (pm) →

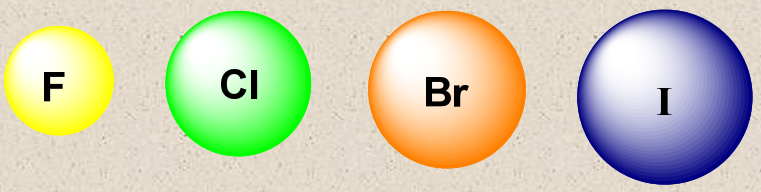


Boiling Points

- For an alkane and a haloalkane of comparable size and shape, **the haloalkane has the higher boiling point.**
  - The **difference is due almost entirely to the greater polarizability** of the three unshared pairs of electrons on halogen compared with the low polarizability of shared electron pairs of covalent bonds.

CH_3CH_3	CH_3Br
bp -89°C	bp 4°C

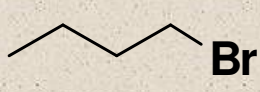
  - Polarizability: A measure of the ease of distortion of the distribution of electron density about an atom in response to interaction with other molecules and ions; fluorine has a very low polarizability, iodine has a very high polarizability.



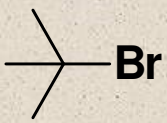
Polarizability: A measure of the ease of distortion of the distribution of electron density

Boiling Points

– Among constitutional isomers, branched isomers have a more compact shape, decreased area of contact, decreased van der Waals attractive forces between neighbors, and lower boiling points.



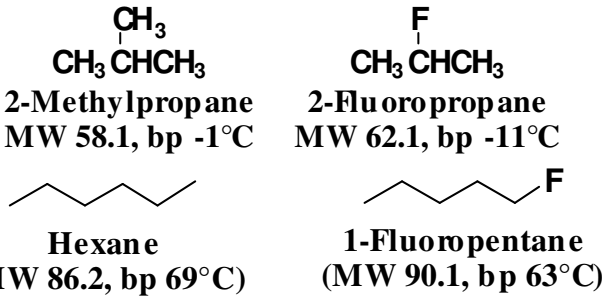
1-Bromobutane
bp 100°C



2-Bromo-2-methylbutane
bp 72°C

Boiling Points

– Boiling points of fluoroalkanes are comparable to those of hydrocarbons of similar molecular weight and shape.



– The low boiling points of fluoroalkanes are the result of the small size of fluorine, the tightness with which its electrons are held, and their particularly low polarizability.

Density

- The densities of liquid haloalkanes are greater than those of hydrocarbons of comparable molecular weight.
  - A halogen has a greater mass per volume than a methyl or methylene group.
- All liquid bromoalkanes and iodoalkanes are more dense than water.
- Di- and polyhalogenated alkanes are more dense than water.

		Density (g/mL) at 25°C		
Haloalkane	X=	Cl	Br	I
CH_2X_2		1.327	2.497	3.325
CHX_3		1.483	2.890	4.008
CX_4		1.594	3.273	4.23

Bond Length & Strengths

C-F bonds are stronger than C-H bonds;
C-Cl, C-Br and C-I bonds are weaker.

Bond	Bond Length (pm)	Bond Dissociation Ethalpy [kJ (kcal)/mol]
C-F	142	464 (111)
C-H	109	414 (99)
C-Cl	178	355 (85)
C-Br	193	309 (78)
C-I	214	228 (57)

Halogenation of Alkanes

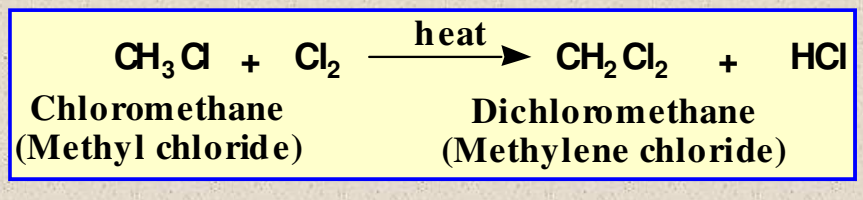
- If a mixture of methane and chlorine is kept in the dark at room temperature, no change occurs.
- If the mixture is heated or exposed to visible or ultraviolet light, reaction begins at once with the evolution of heat.

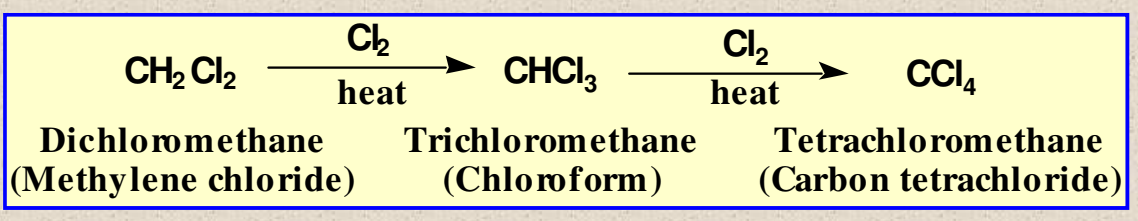
$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{\text{heat}} \underset{\substack{\text{Chloromethane}\\ \text{(Methyl chloride)}}}{CH_3Cl} + HCl \qquad \Delta H^0 = \text{-100 kJ (23.9 kcal)/mol}$$

- Substitution: A reaction in which an atom or group of atoms is replaced by another atom or group of atoms.

Halogenation of Alkanes

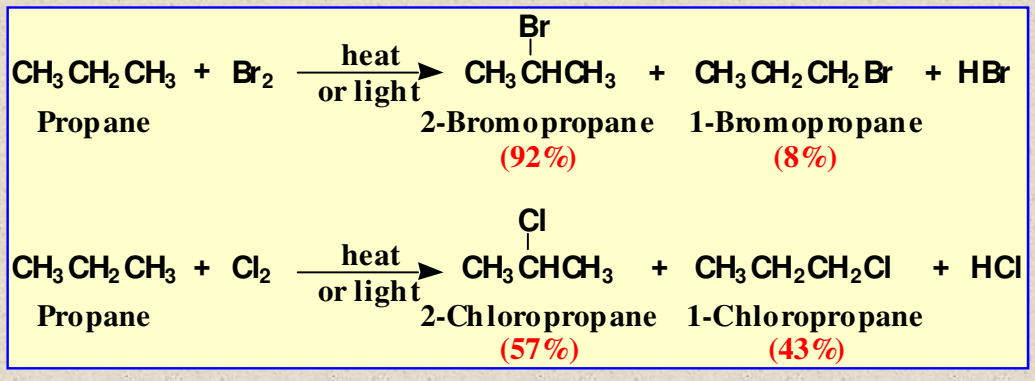
– If chloromethane is allowed to react with more chlorine, a mixture of chloromethanes is formed.





Regioselectivity

Regioselectivity is high for **bromination**, but **chlorination** is NOT as selective



Energetics

- Bond Dissociation Enthalpies (BDE)

Hydrocarbon	Radical	Name of Radical	Type of Radical	ΔH^0 kJ(kcal)/mol
$CH_2=CHCH_2-H$	$CH_2=CHCH_2\cdot$	Allyl	Allylic	372 (89)
$C_6H_5CH_2-H$	$C_6H_5CH_2\cdot$	Benzyl	Benzylic	376 (90)
$(CH_3)_3C-H$	$(CH_3)_3C\cdot$	*tert*-Butyl	3°	405 (97)
$(CH_3)_2CH-H$	$(CH_3)_2CH\cdot$	Isopropyl	2°	414 (99)
CH_3CH_2-H	$CH_3CH_2\cdot$	Ethyl	1°	421 (101)
CH_3-H	$CH_3\cdot$	Methyl	Methyl	439 (105)
$CH_2=CH-H$	$CH_2=CH\cdot$	Vinyl	Vinylic	464 (111)

Increasing Stability

Increasing E

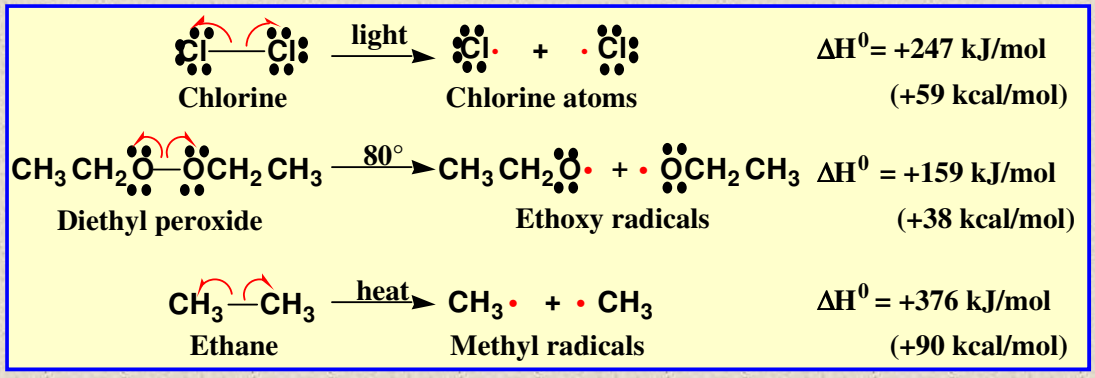
Mechanisms

Radical: any chemical species that contains one or more unpaired electrons.

- Radicals are formed by homolytic bond cleavage.
- The order of stability of alkyl radicals is 3° > 2° > 1° > methyl.

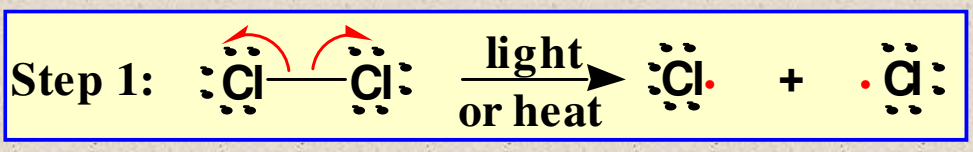
Mechanisms

– The order of stability of alkyl radicals is 3° > 2° > 1° > methyl.



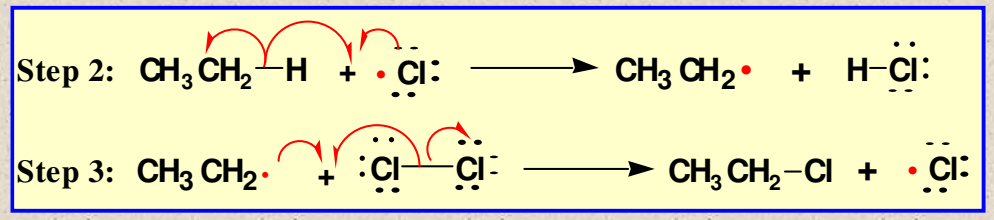
Radical Chain Mechanism

Chain initiation: A step in a chain reaction characterized by formation of reactive intermediates (radicals, anions, or cations) from nonradical or noncharged molecules.



Radical Chain Mechanism

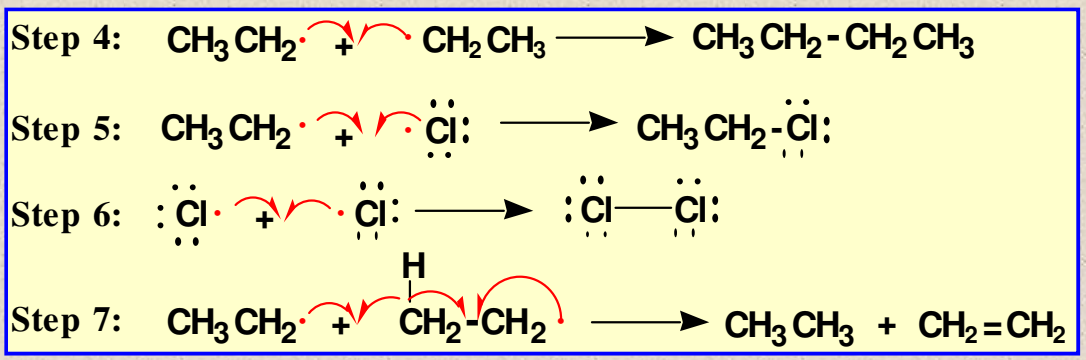
- **Chain propagation:** A step in a chain reaction characterized by the reaction of a reactive intermediate and a molecule to form a new radical or reactive intermediate and a new molecule.



- **Chain length:** The number of times the cycle of chain propagation steps repeats in a chain reaction.

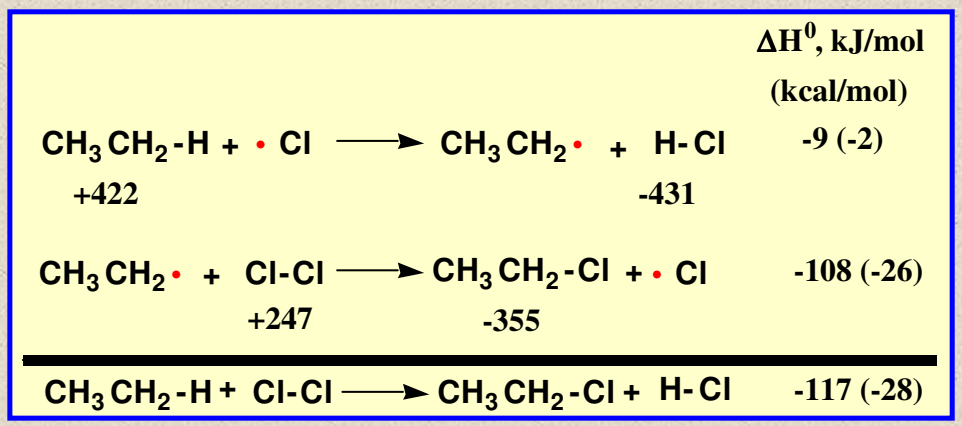
Radical Chain Mechanism

- **Chain termination:** A step in a chain reaction that involves destruction of reactive intermediates.



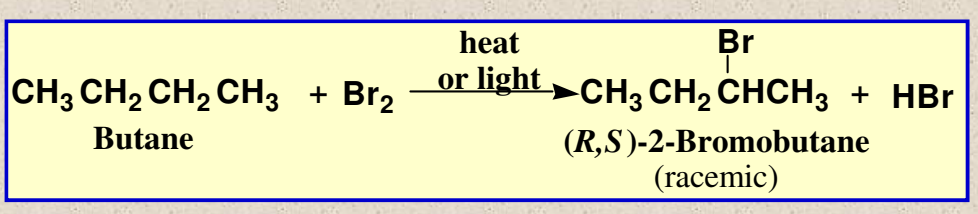
Chain Propagation Steps

- For any set of chain propagation steps, their
  - equations add to the observed stoichiometry.
  - enthalpies add to the observed ΔH^0.



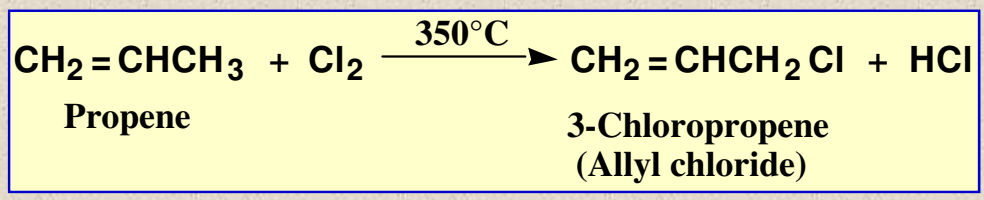
Stereochemistry

- When radical halogenation produces a chiral center or takes place at a hydrogen on a chiral center, the product is a racemic mixture of *R* and *S* enantiomers.

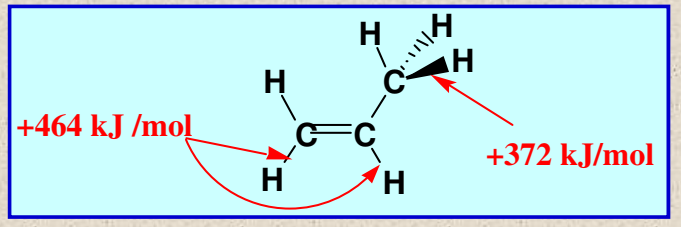


Allylic Halogenation

- Allylic carbon: A C atom adjacent to a C-C double bond.
- Allylic hydrogen: An H on an allylic carbon.

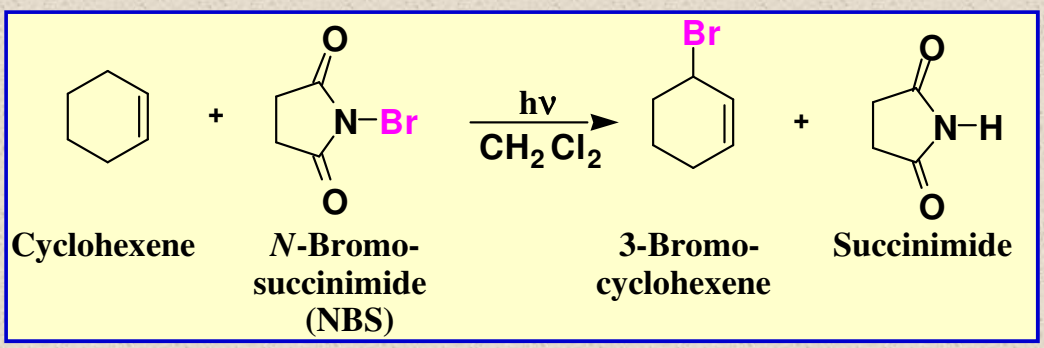


– an allylic C-H bond is weaker than a vinylic C-H bond.



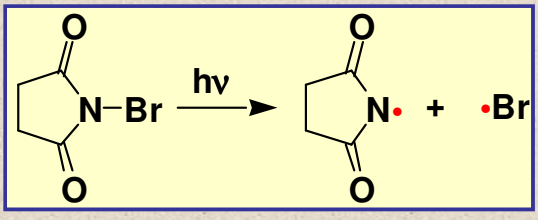
Allylic Bromination

Allylic bromination using NBS:



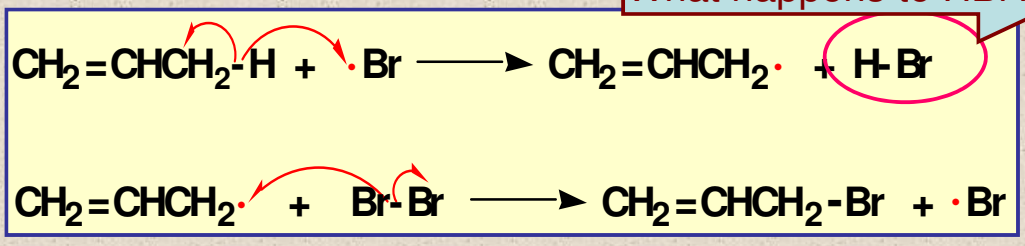
Allylic Bromination

- A radical chain mechanism
  - Chain initiation



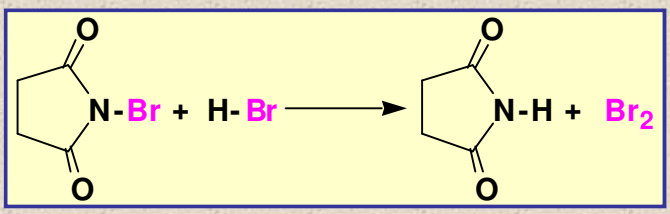
  - Chain propagation

What happens to HBr?

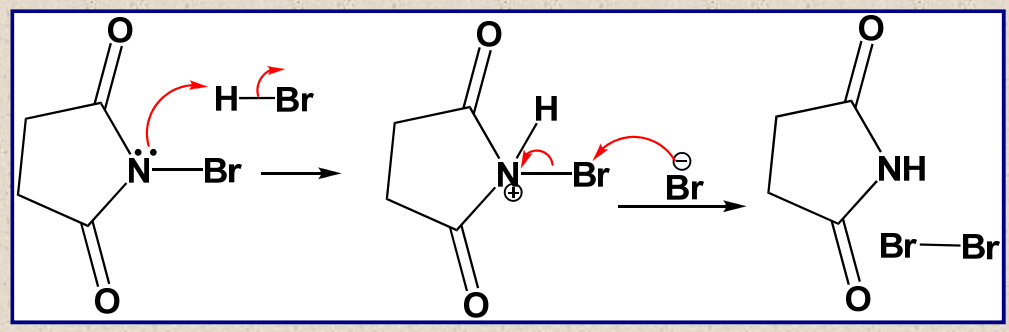


Allylic Bromination

NBS neutralizes HBr and the protonated amide then provides Br_2 for the chain process:

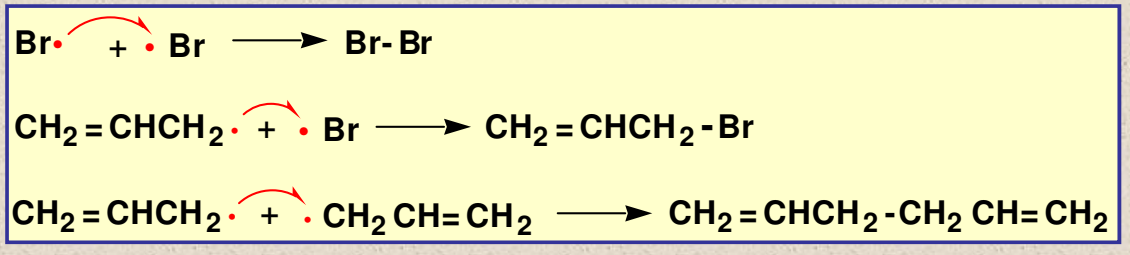


Mechanism:



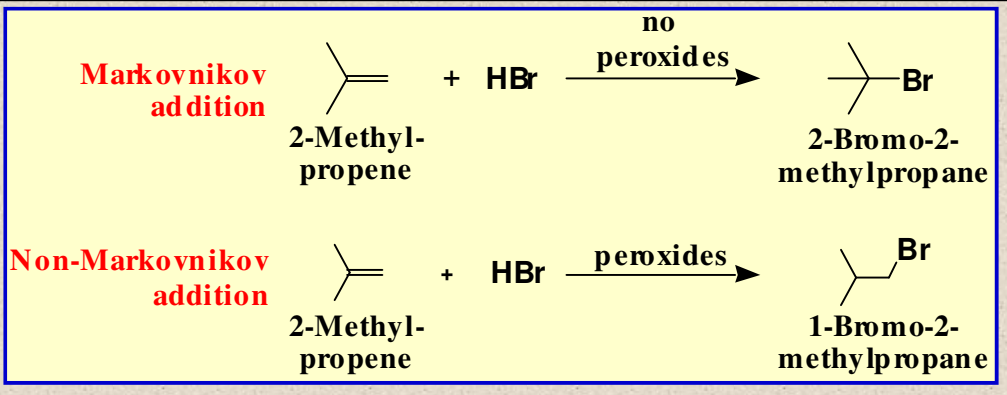
Allylic Bromination

–chain termination



Radical Addn of HBr to Alkenes

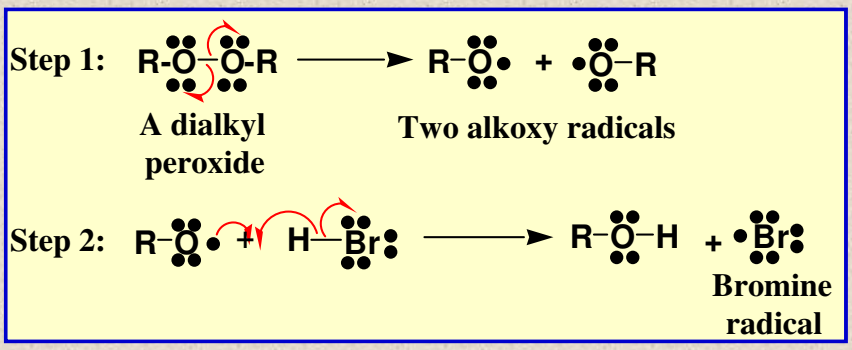
- Addition of HBr to alkenes gives either Markovnikov addition or non-Markovnikov addition depending on reaction conditions.
  - Markovnikov addition occurs when radicals are absent.
  - non-Markovnikov addition occurs when peroxides or other sources of radicals are present.



Radical Addn of HBr to Alkenes

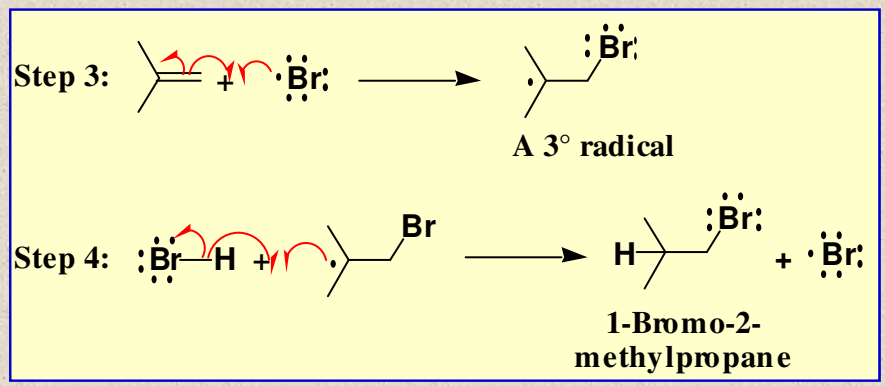
- Addition of HCl and HI gives only Markovnikov products.
- To account for the the non-Markovnikov addition of HBr in the presence of peroxides, a radical chain mechanism is proposed--

- Chain initiation:



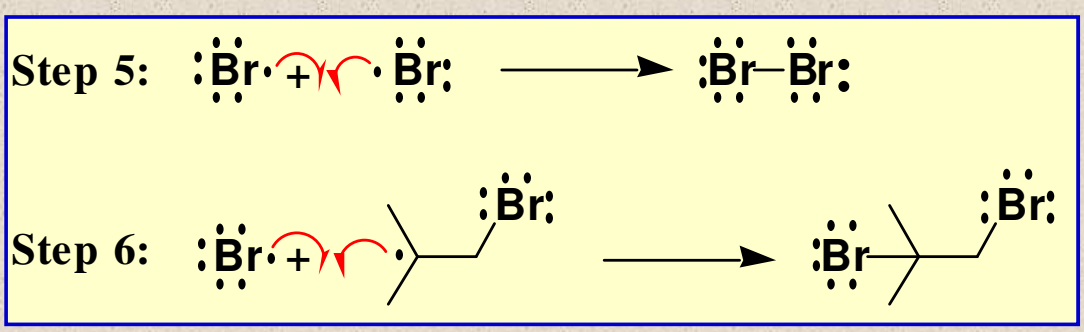
Radical Addn of HBr to Alkenes

- Chain propagation:



Radical Addn of HBr to Alkenes

- Chain termination:



Radical Addn of HBr to Alkenes

This pair of reactions illustrates how the products of a reaction can be changed by a change in experimental conditions:

- **Polar addition** of HBr is regioselective, with protonation of the alkene preceding the addition of Br^- to the **more** substituted carbon.
- **Radical addition** of HBr is also regioselective, with Br atom adding to the **less** substituted carbon.