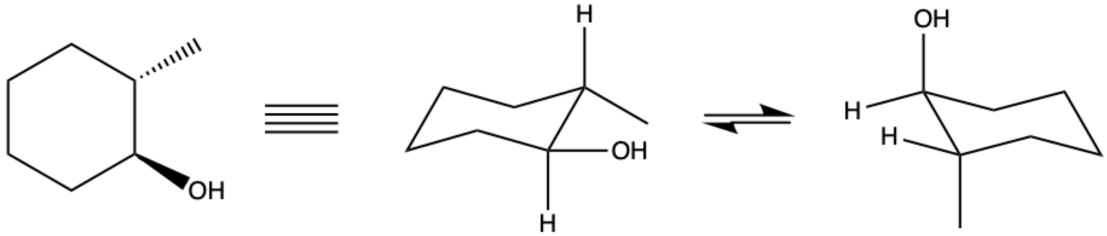
CHEM 261 October 4, 2022

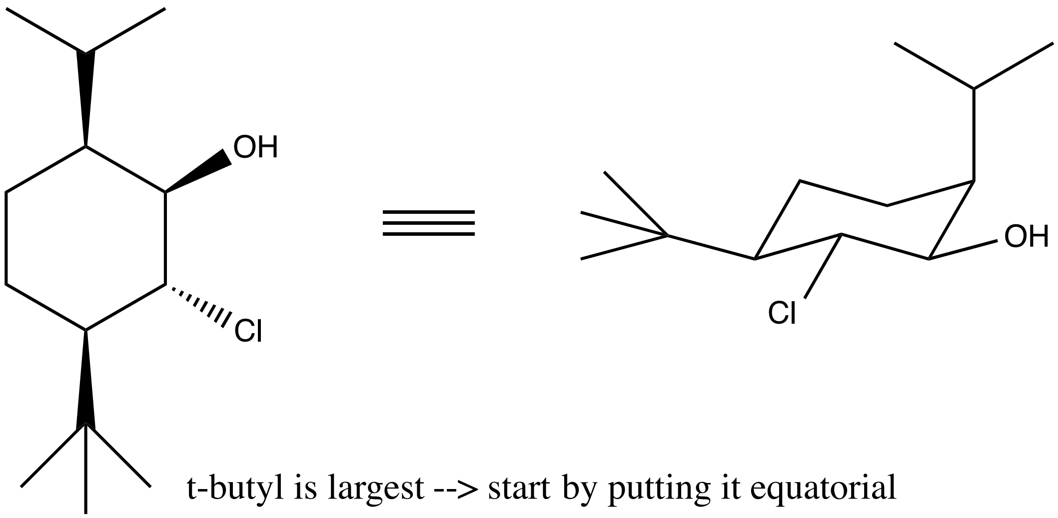
Recall: Cyclohexane molecules exist as chair conformations. Steric strain drives the lowest energy conformation.

Ex1)



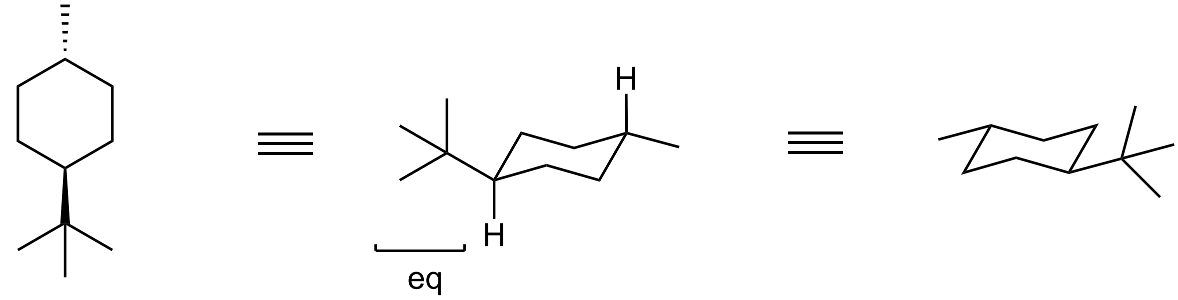
Lowest energy conformation

Ex2)

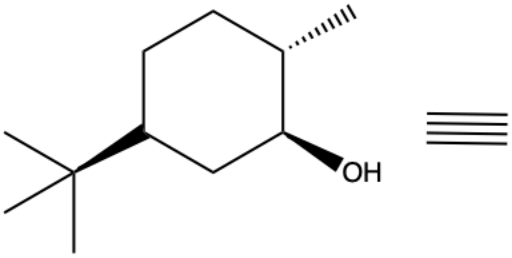


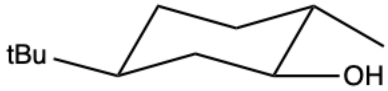
t-butyl is largest --> start by putting it equatorial

Ex3)

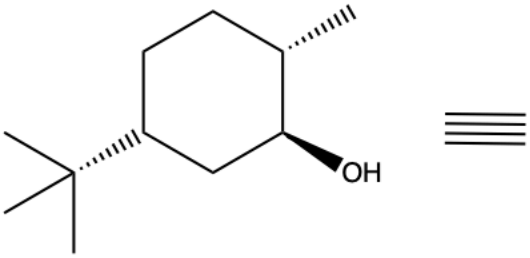


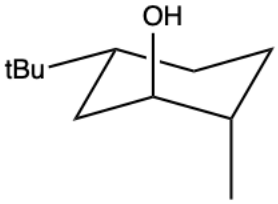
Ex4)





Lowest energy conformation

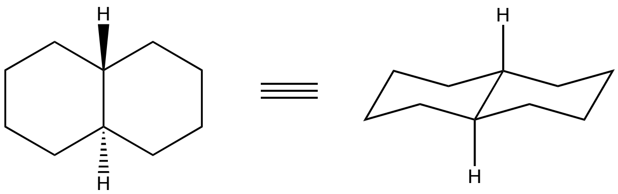




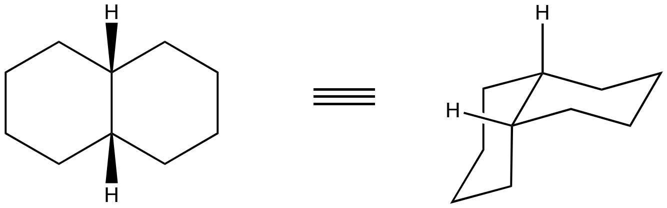
Lowest energy conformation

Examples of Basic Bicyclic Compounds:

trans-Decalin: ($C_{10}H_{18}$)

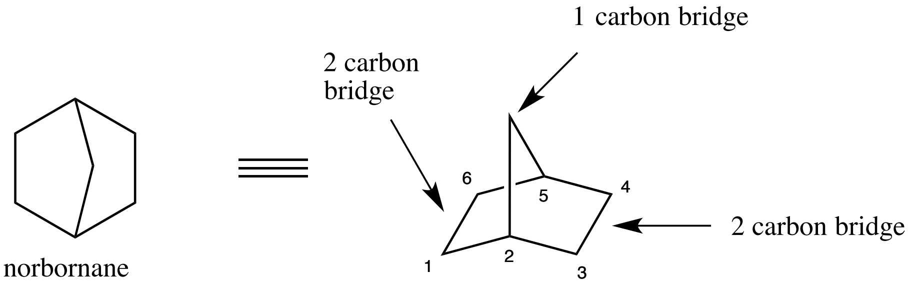


cis-Decalin:



Stereoisomers

2 degrees of unsaturation

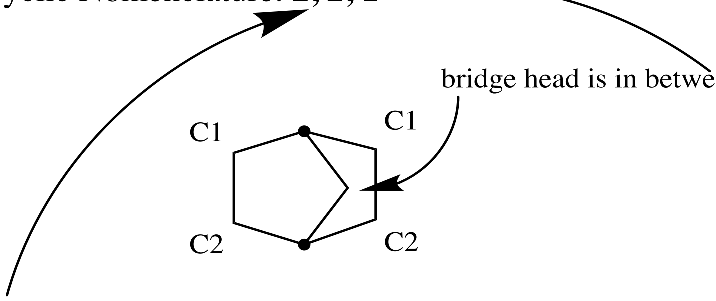


norbornane
C_7H_{12}
Degrees of unsaturation: 2

2 bridge head carbons (2 and 5)
6 membered ring in a boat conformation

You are **not** responsible for nomenclature of bridged bicyclic compounds described below, but you should know norbornane and decalin structures above

Bicyclic Nomenclature: **2, 2, 1**

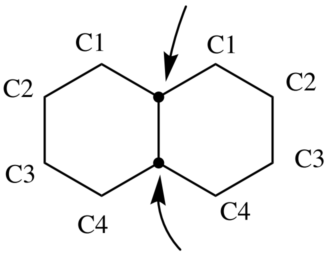


bridge head is in between 1 carbon

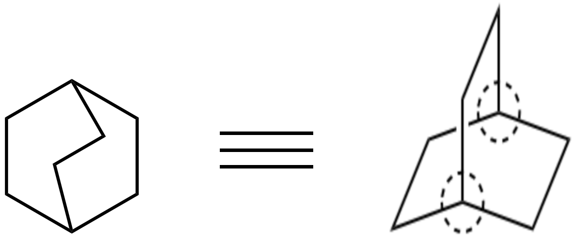
there are two sets of two carbons (C1, C2) on both sides of the bridge head, hence, 2, 2

Bicyclic Nomenclature: **4, 4, 0**

bridge heads in position 0

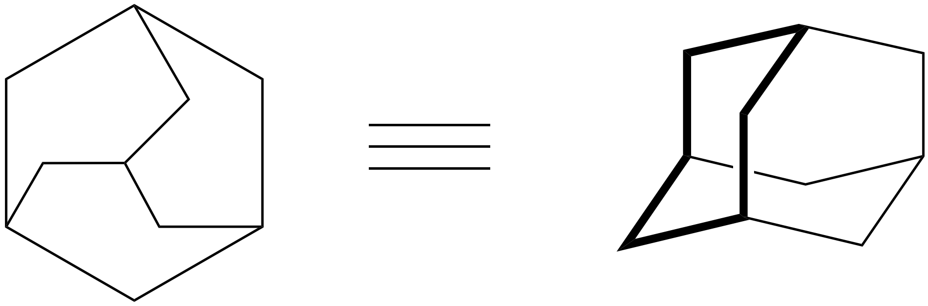


bridge heads in position 0



2,2,2-Bicyclooctane

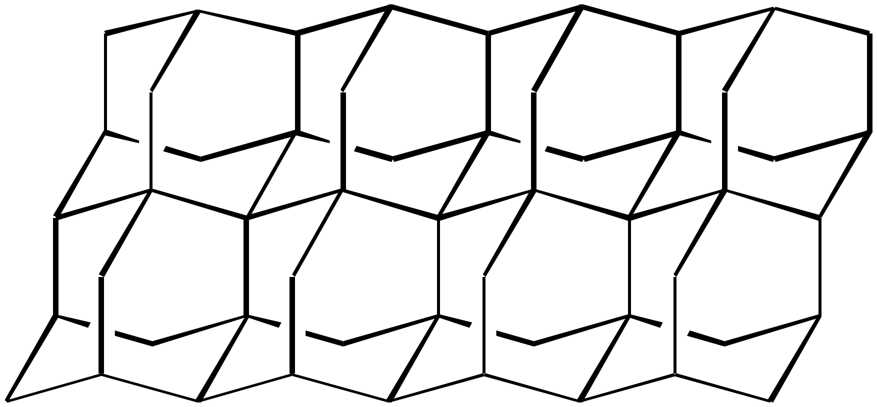
A tricyclic compound:



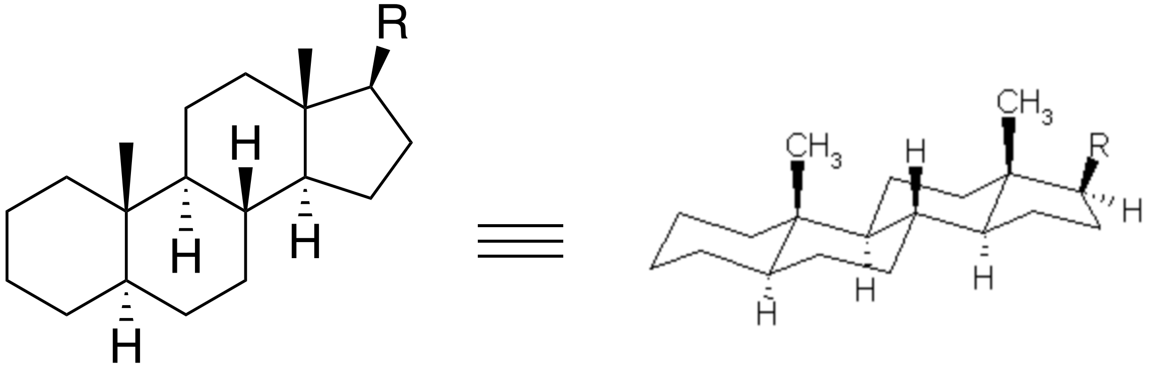
Adamantane

- This will be the basic structure of diamond

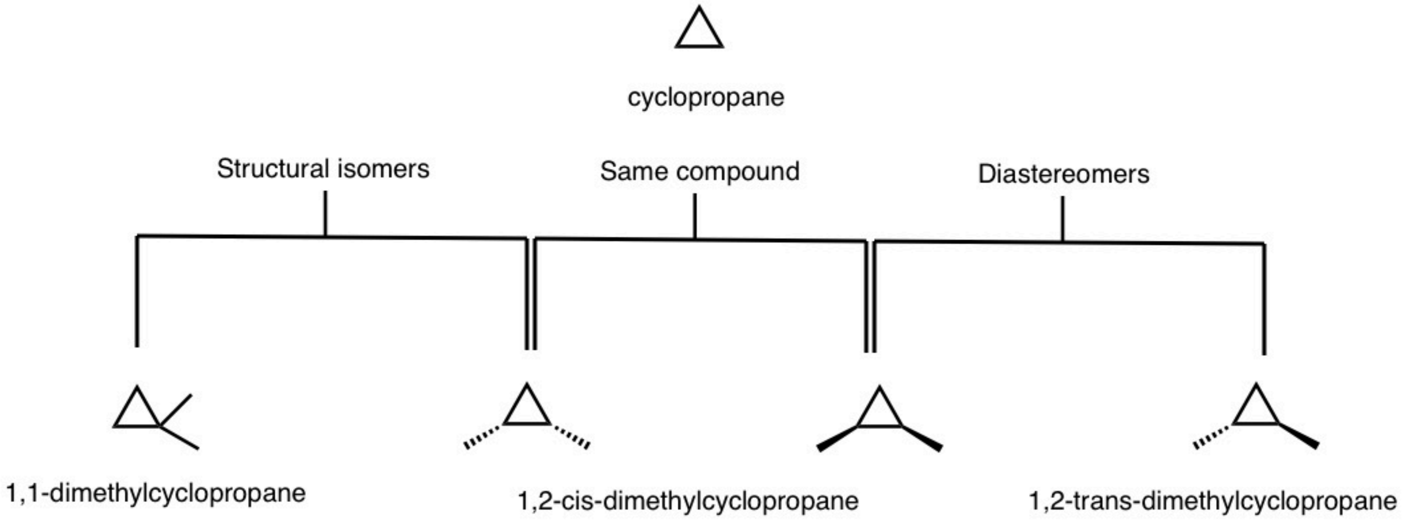
Diamond:



Steroids:



Cyclopropane



When naming the compounds above, it is necessary to describe the location of the two methyl groups even if they are located on the same substituent because all of these are dimethylcyclopropanes (i.e. from left to right: **1,1**-dimethyl-, **1,2-cis-**dimethyl-, **1,2-trans**-dimethyl- cylcopropane).

Reactions of alkanes

1) **Combustion:**

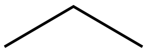
$$\text{R-H} \quad + \quad O_2 \quad \xrightarrow{\Delta=\textbf{heat}} \quad CO_2 \quad + \quad H_2O$$

R = any alkyl group

General formula for combustion reactions:

$$C_nH_{2n+2} + \left(\frac{3n}{2} + \frac{1}{2}\right) O_2 \quad \longrightarrow \quad (n+1)\ H_2O + n\ CO_2$$

e.g. propane



$CH_3CH_2CH_3$ $\quad 5O_2 \quad \xrightarrow{\Delta} \quad 3CO_2 \quad + \quad 4H_2O$

2) Halogenation of alkanes

$$\text{R-H} + X_2 \xrightarrow{\mathbf{h\nu}} \text{R-X} + \text{HX}$$

R = any alkyl group, R-X = alkyl halide / haloalkane (
X = halogen
F_2 (most reactive) > Cl_2 > Br_2 >> I_2 (does not react)
h = Planck's constant 6.6 $\times10^{-34}$ joules-sec
ν = frequency of light
E = **$h\nu$, are the symbols we use to describe light energy**

In this course, we will be focused on chlorination and bromination.

Substitution reaction (via radicals) – Substitute H with X

e.g. Chlorination of methane

$$CH_4 + Cl_2 \xrightarrow{h\upsilon} CH_3Cl + HCl$$

methane

methyl chloride
chloromethane

$$CH_3Cl + Cl_2 \xrightarrow{h\upsilon} CH_2Cl_2 + HCl$$

methylene chloride
dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\upsilon} CHCl_3 + HCl$$

chloroform
trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow{h\upsilon} CCl_4 + HCl$$

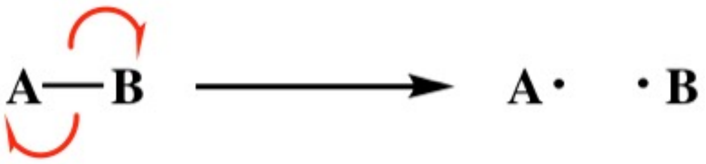
carbon tetrachloride
tetrachloromethane

Mechanism of reaction:

- Step by step description (proposal) of a reaction process (hypothetical and difficult to "prove")

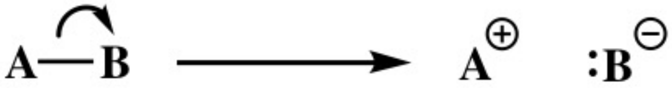
Two kinds of mechanism

1. **Homolytic** (radical): One electron goes to each atom once the bond in broken. e.g. Free radical halogenation of alkanes



The red half arrows above describe the movement of one electron, full arrows describe movement of lone pairs.

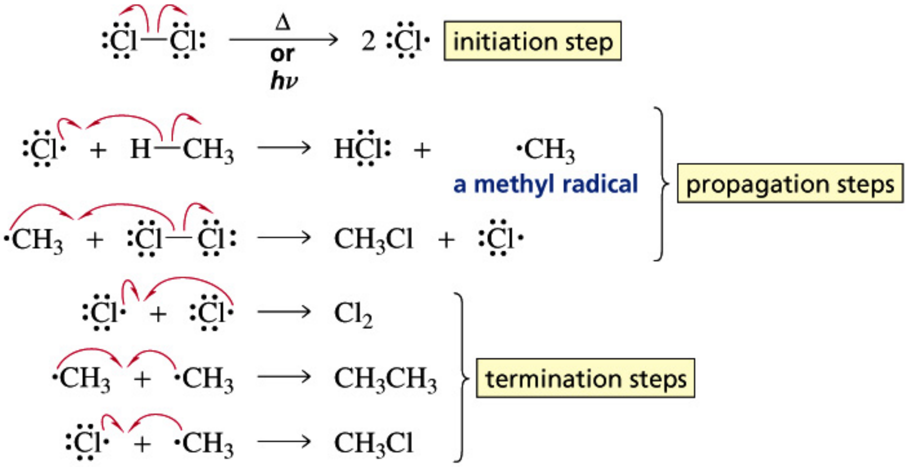
2. **Heterolytic** (polar reaction): The electron pair goes to one of the atoms once the bond is broken. e.g. Addition reactions of alkenes; elimination reactions



Homolytic reactions are less common than heterolytic reactions
- Initiated by heat (Δ) or by light (hυ)

Mechanism of halogenation of CH_4:

$$CH_4 + X_2 \xrightarrow{h\upsilon} CH_3X + HX$$



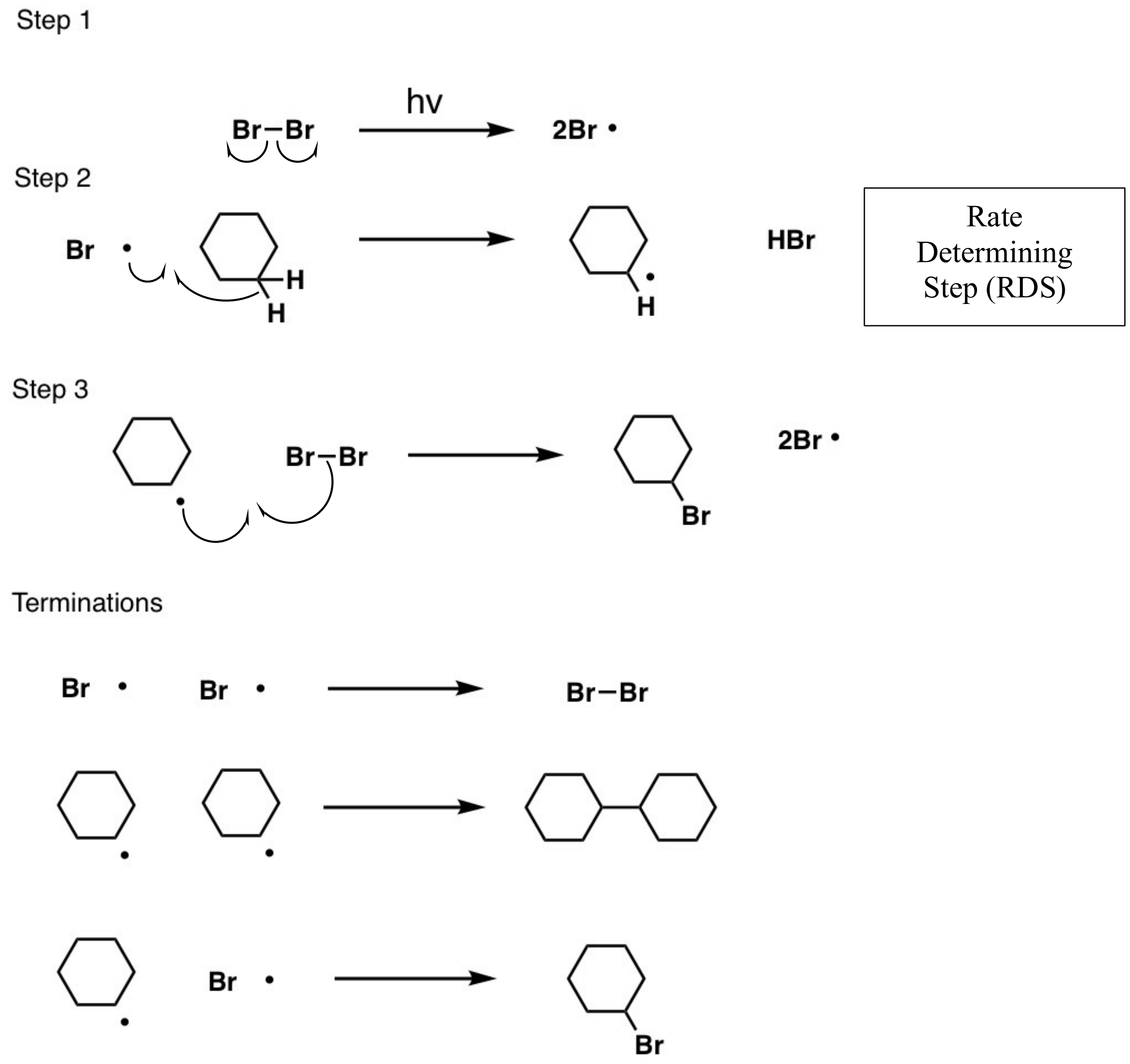
Propagation is the main step within the process. The termination step is the combination of radicals and is quite rare during the progress of the reaction, yet any one of the three listed can occur to terminate the reaction.

Note: The above mechanism also applies to other halogens (F, Cl, Br; not I)

Example: Ethane (analogous)

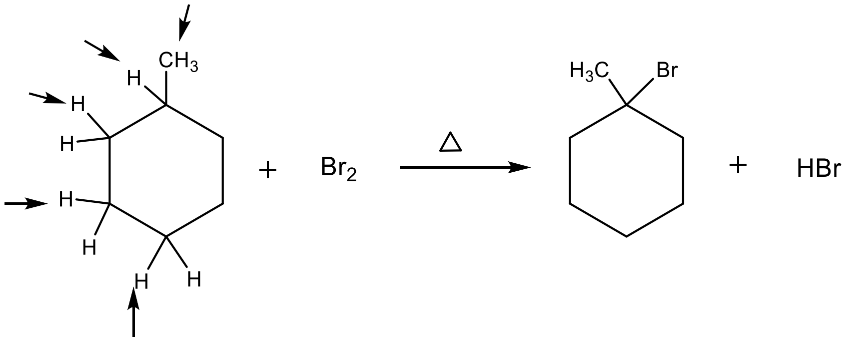
$$H_3C - CH_3 \xrightarrow[h\nu]{Cl_2} CH_3\text{-}CH_2\text{-}Cl \;+\; HCl$$

Example: Bromination of cyclohexane
(step 1 is **initiation**, steps 2 and 3 are **propagation steps** that are the main process. Other steps are **termination** steps that shut down the reaction



Rate Determining Step (RDS)

Example: Methylcyclohexane

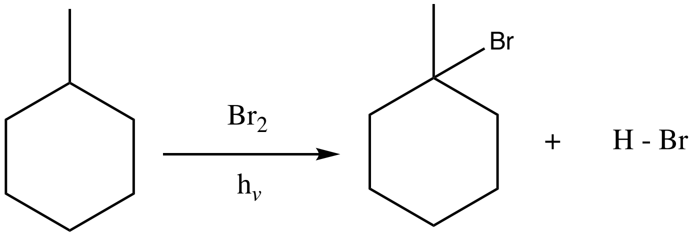


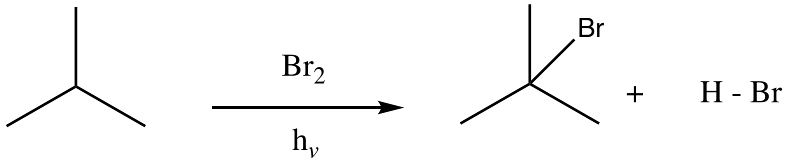
The reaction can utilize either heat (Δ) or light (hν)

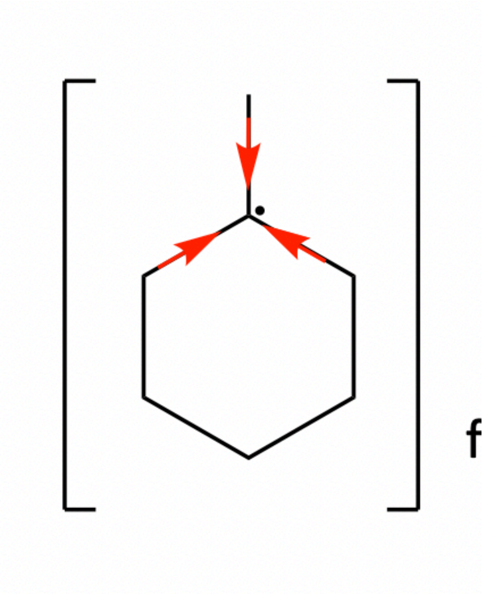
Different types of hydrogen can be pulled from a methylcyclohexane in a radical halogenation reaction to give various products. However, one main product is obtained. This is explained in terms of the stability of the radical formed during the reaction process.

Other Examples:

Alkyl Groups Donate electrons and stabilize
Intermediate Radical
is NOT a transition state

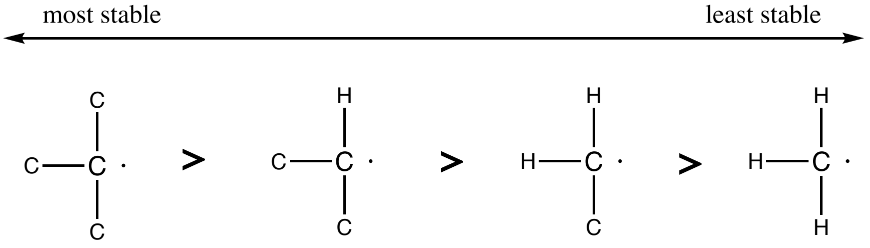






Stability of radicals:

- Stability increases with alkyl substitution
- Alkyl groups are polarizable and donate electrons to electron deficient sites better than hydrogens (this is called **inductive effect** and occurs through sigma bonds)



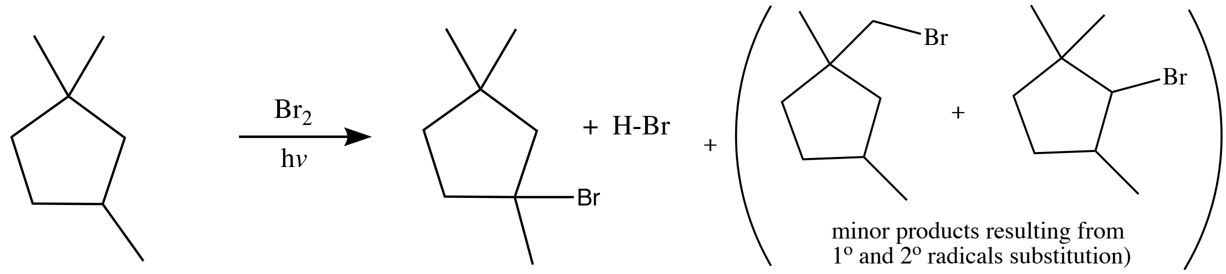
tertiary (3°) radical	secondary (2°) radical	primary (1°) radical	methyl radical

Or it can be summarized from least to most stable radicals:

$^{\cdot}CH_3$	<	$^{\cdot}CH_2R$	<	$^{\cdot}CHR_2$	<	$^{\cdot}CR_3$
methyl radical (least stable)		primary (1°) radical		secondary (2°) radical		tertiary (3°) radical (most stable)

More Examples

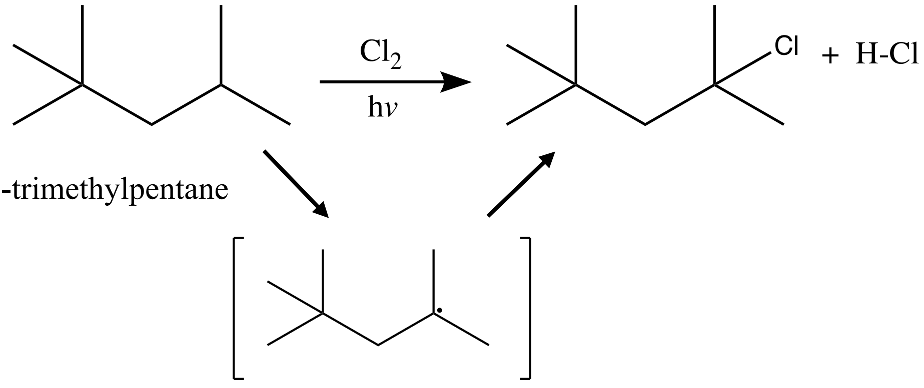
A. 1,1,3-trimethylcyclopentane bromination



minor products resulting from 1° and 2° radicals substitution)

1,1,3-trimethylcyclopentane

B. 2,2,4-trimethylpentane chlorination



2,2,4-trimethylpentane

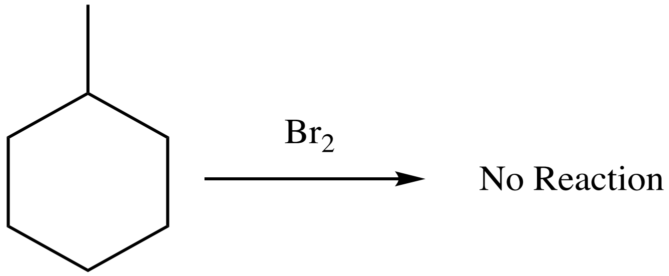
intermediate

<u>RECALL:</u>

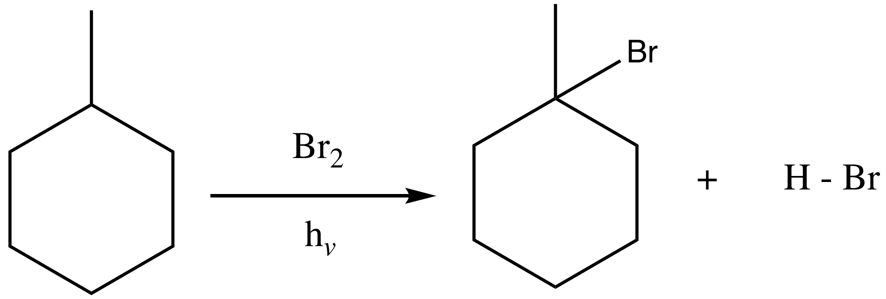
Halogenation of alkanes:

- requires light or heat to cause a reaction between the starting material and halogen.

Example:

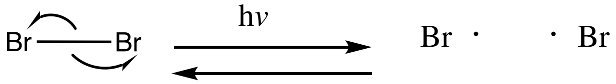


- requires light or heat to cause a reaction between the starting material and halogen.

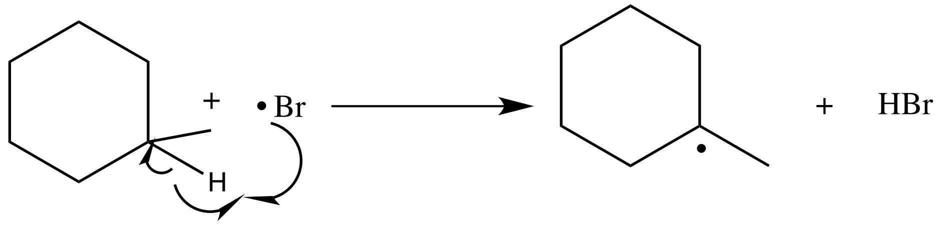


C_7H_{14}

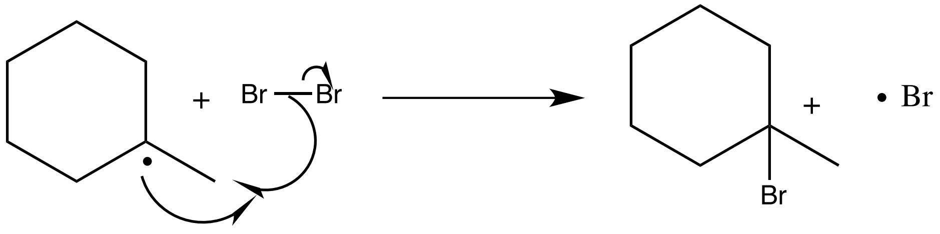
Initiation Step:



Propagation Step 1

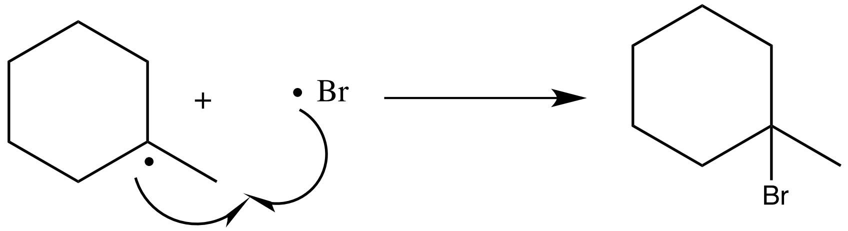


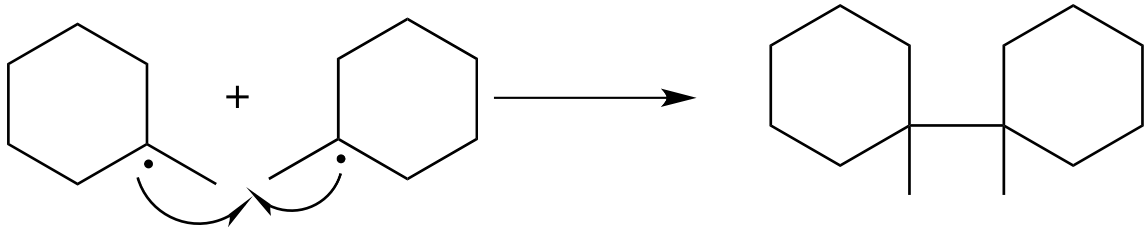
Propagation Step 2



Termination Step: Radicals Recombine

-Very minor component of the reaction



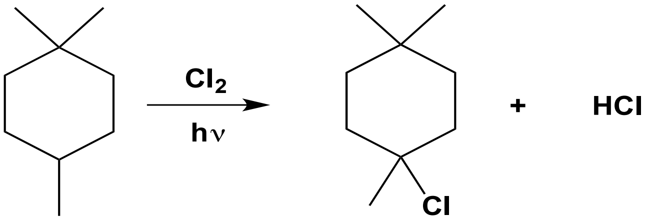


Two alkyl radicals combining is highly unlikely because the chances of them finding one another is very low (they are low in concentration) – above also very crowded (steric effect)

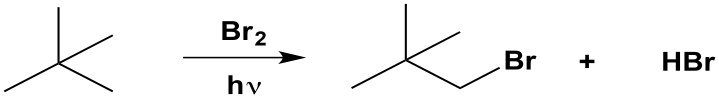
Stability of radicals:

- Stability increases with alkyl substitution
- Alkyl groups are polarizable and donate electrons to electron deficient sites better than hydrogens (this is called **inductive effect** and occurs through sigma bonds)

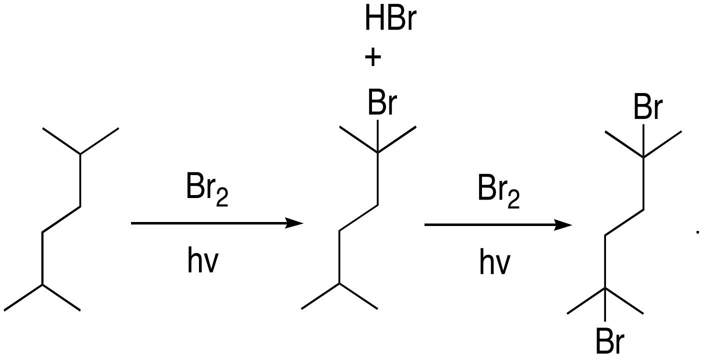
More Examples:



1,1,4-trimethylcyclohexane



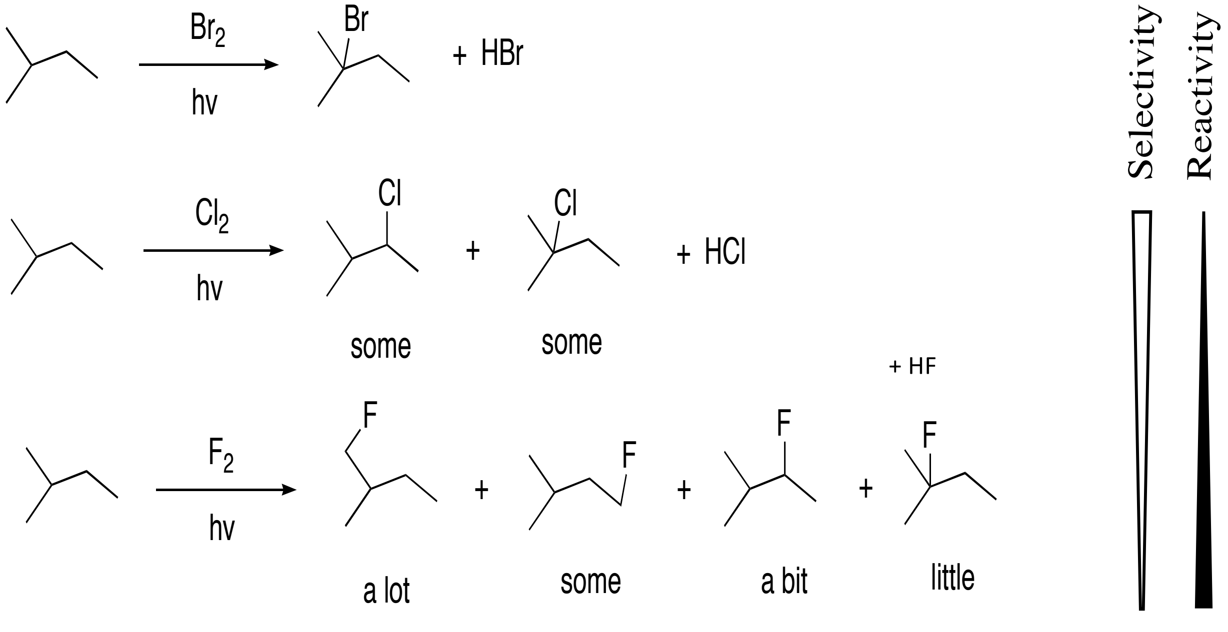
Neopentane
(2,2-dimethylpropane)



2, 5-dimethylhexane

<u>Reactivity and Selectivity (Hammond Postulate)</u>

e.g. Halogenation of 2-methylbutane



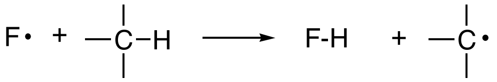
NOTE:

More reactive reagents give less selective products
Less reactive reagents give more selective products

I_2 does not react as above

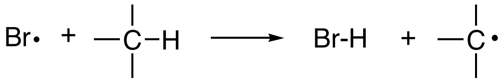
Reactivity TREND:

$F_2 > Cl_2 > Br_2 >> I_2$ Iodine does not react



$$F\cdot + -\overset{|}{\underset{|}{C}}-H \longrightarrow F\text{-}H + -\overset{|}{\underset{|}{C}}\cdot$$

ΔH = -35 kcal/mole
Exothermic



$$Br\cdot + -\overset{|}{\underset{|}{C}}-H \longrightarrow Br\text{-}H + -\overset{|}{\underset{|}{C}}\cdot$$

ΔH = +16 kcal/mole
Endothermic

Selectivity TREND:

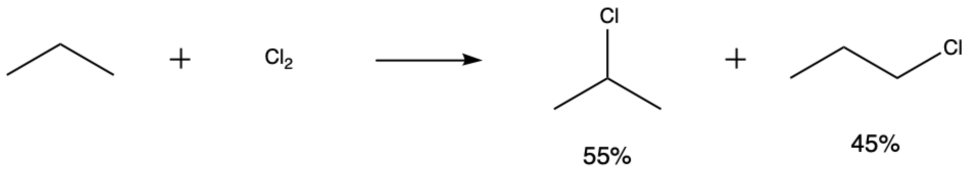
$Br\cdot > Cl\cdot > F\cdot$

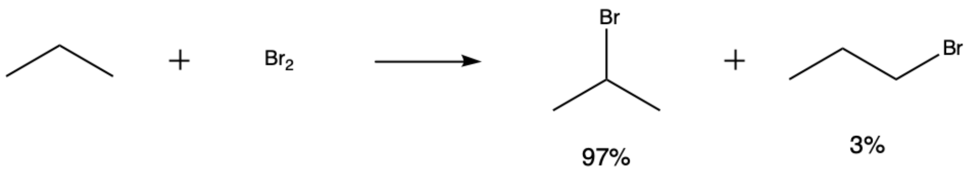
most selective	least selective
endothermic	exothermic

Bromine atom "searches" the molecule to create the most stable radical
Fluorine atom is small and feels the loss of an electron much more than bromine

- Fluorine is less precise and reacts immediately

Example:





Chlorine is more reactive but less selective than bromine

For Exothermic Reactions

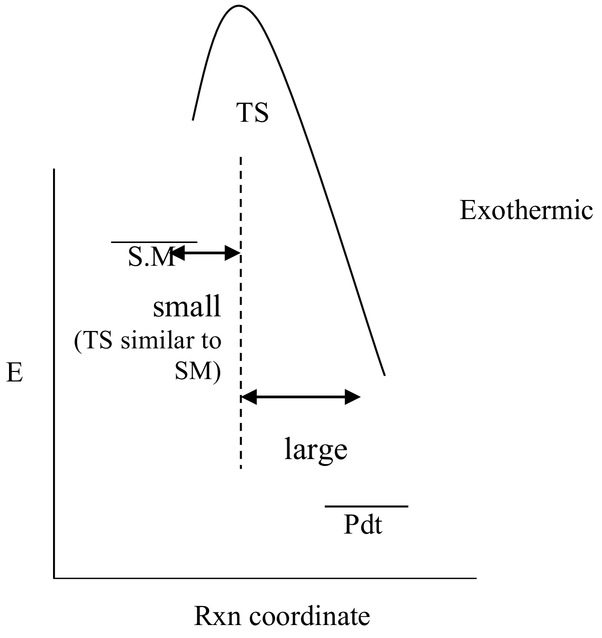
-The transition state (TS) resembles the starting material (SM)
- Less selective reaction because of a small difference in Ea

For Endothermic Reactions

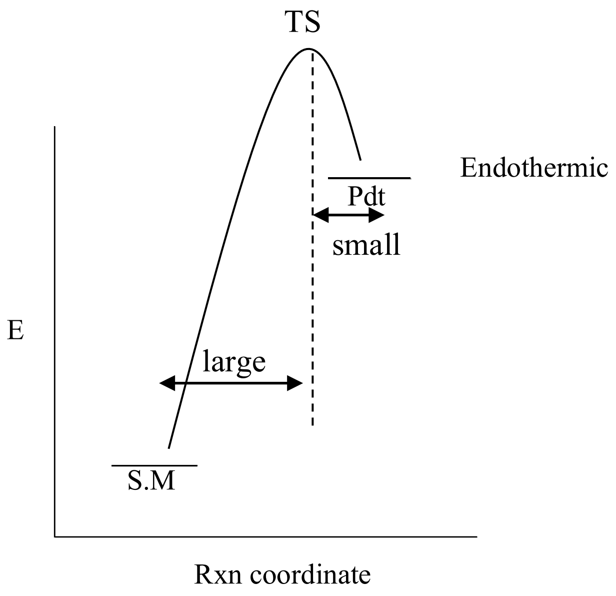
-The transition state (TS) resembles the products (Pdt)
- More selective because of a larger difference in Ea

Energy Diagrams for Halogenation Reactions

Fluorination (ΔH < 0)



Bromination (ΔH > 0)



E = energy
TS = transition state
SM = starting material

Naming of Alkyl Halides = Haloalkanes

REACTIONS OF ALKANES

COMBUSTION

$$R-H + O_2 \xrightarrow{\Delta} CO_2 + H_2O$$

$$+ 5\,O_2 \xrightarrow{\Delta} 3CO_2 + 4H_2O$$

C_3H_8

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

HALOGENATION

heat

$$R-H + X_2 \xrightarrow[\text{OR } h\nu]{\Delta} R-X + HX$$

light

R = alkyl

X = halogen

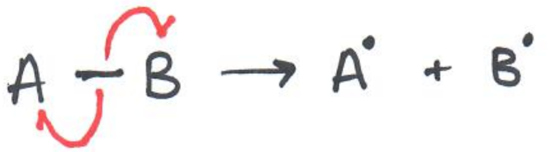
$E = h\nu$ ← frequency.

↑ Planck's constant

$$F_2 > Cl_2 > Br_2 \gg I_2$$

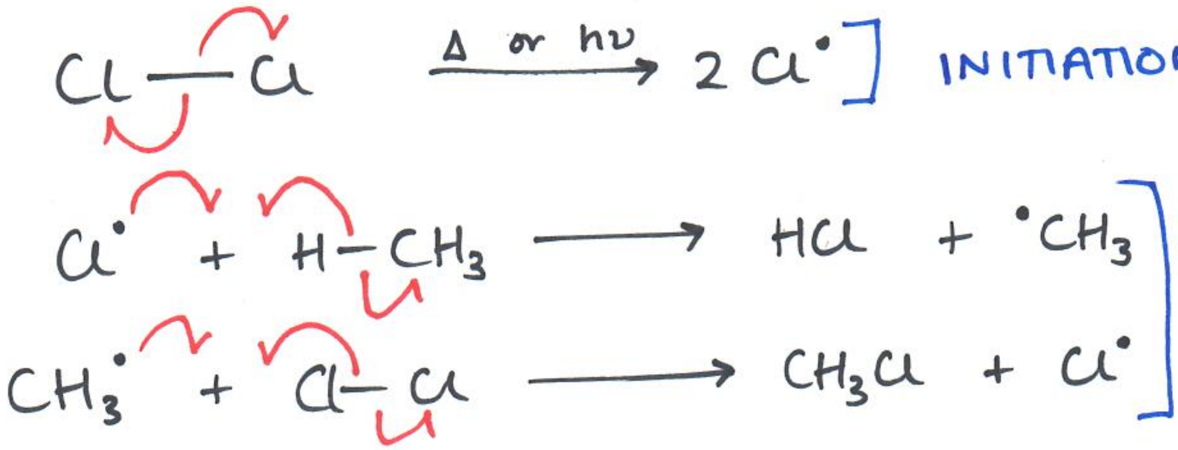
↑ does not react!

Breaking bonds:

HOMOLYTIC	HETEROLYTIC
 $A-B \rightarrow A^{\bullet} + B^{\bullet}$	 $A-B \longrightarrow A^{\oplus} + B^{\ominus}$
Radical reactions	Polar reactions
→ single electron	→ pair of electrons

Radical substitution:

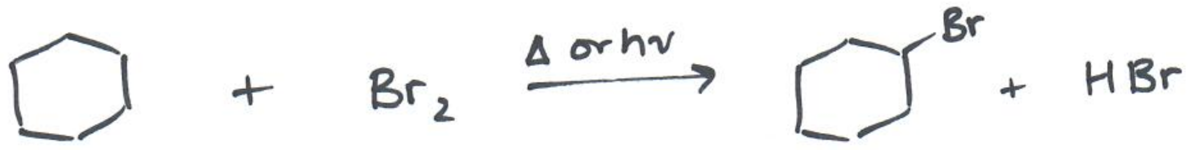
$$CH_4 + Cl_2 \xrightarrow{\Delta \text{ or } h\nu} CH_3Cl + HCl$$

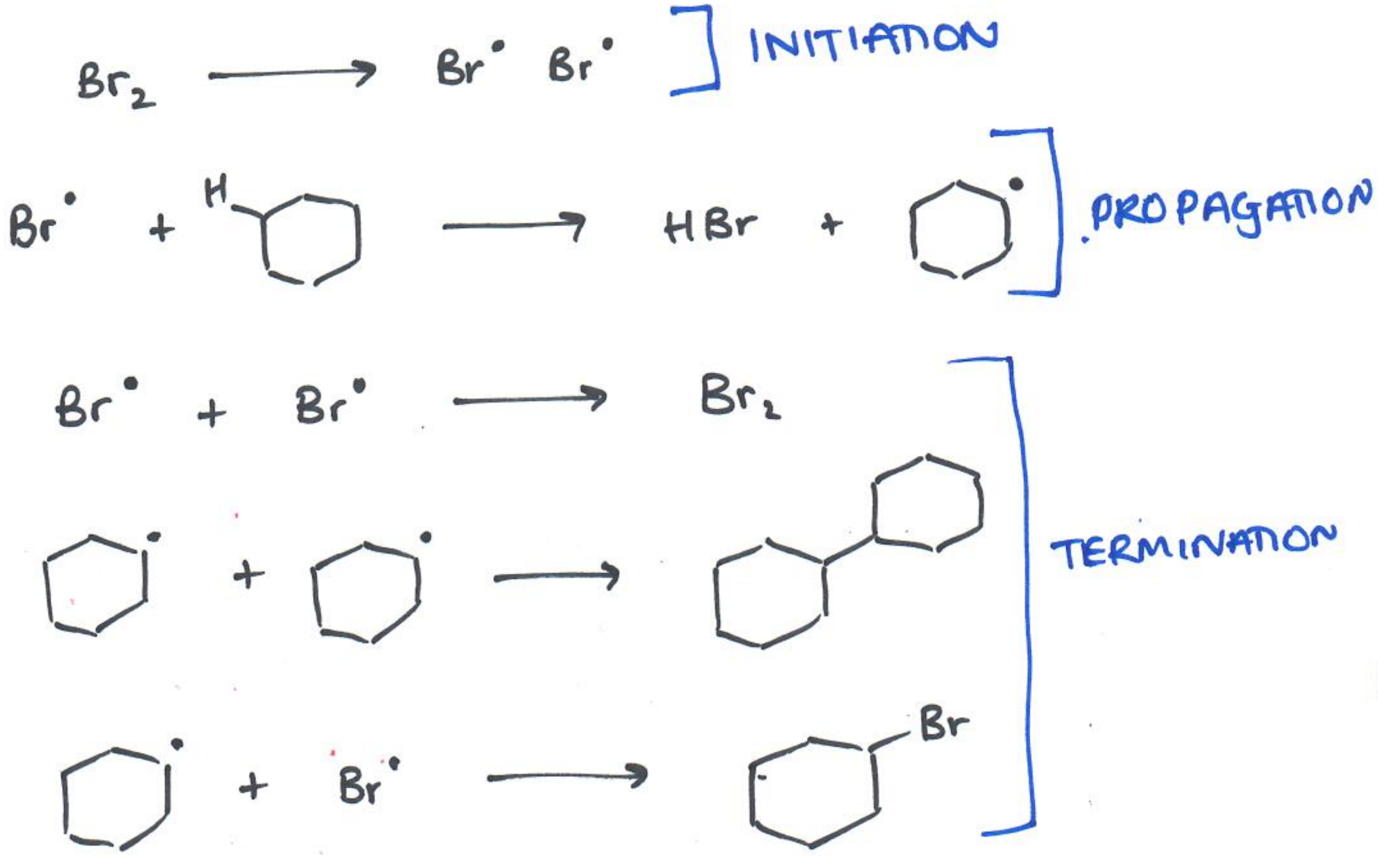


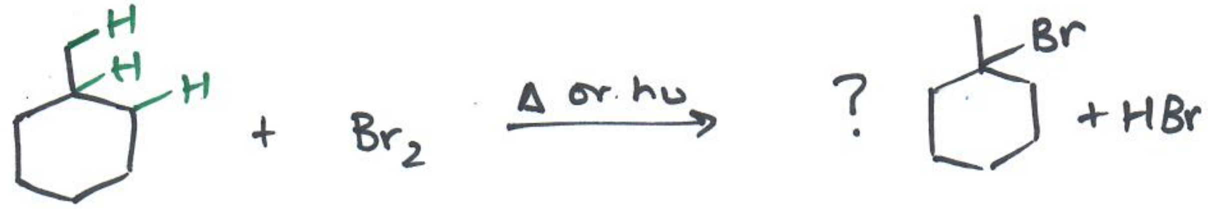
$$Cl-Cl \xrightarrow{\Delta \text{ or } h\nu} 2\,Cl^{\bullet}$$ INITIATION

$$Cl^{\bullet} + H-CH_3 \longrightarrow HCl + {}^{\bullet}CH_3$$
$$CH_3^{\bullet} + Cl-Cl \longrightarrow CH_3Cl + Cl^{\bullet}$$ PROPAGATION

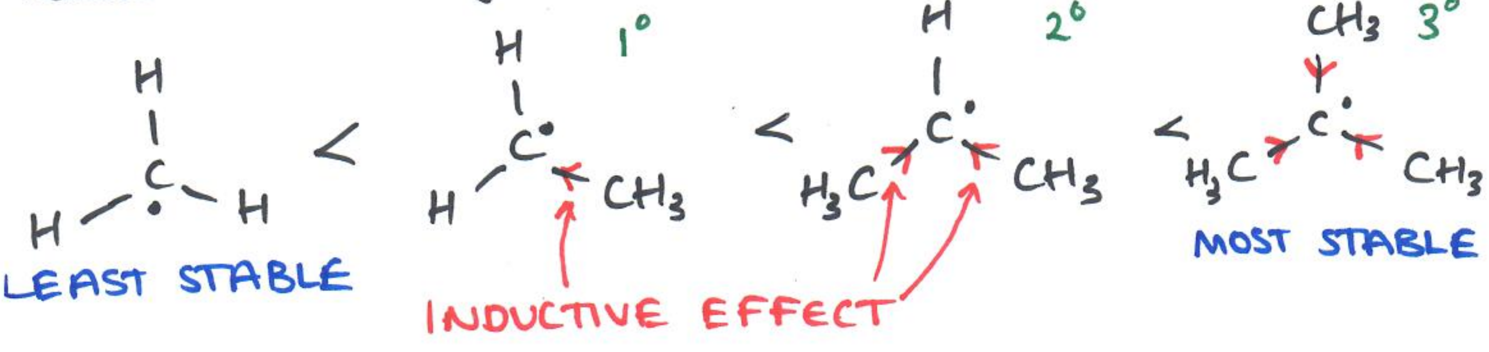
$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl-Cl$$
$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3-CH_3$$
$$Cl^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3Cl$$ TERMINATION

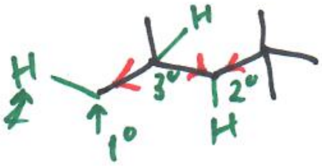




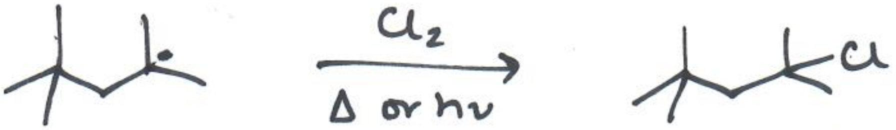


Radical stability:

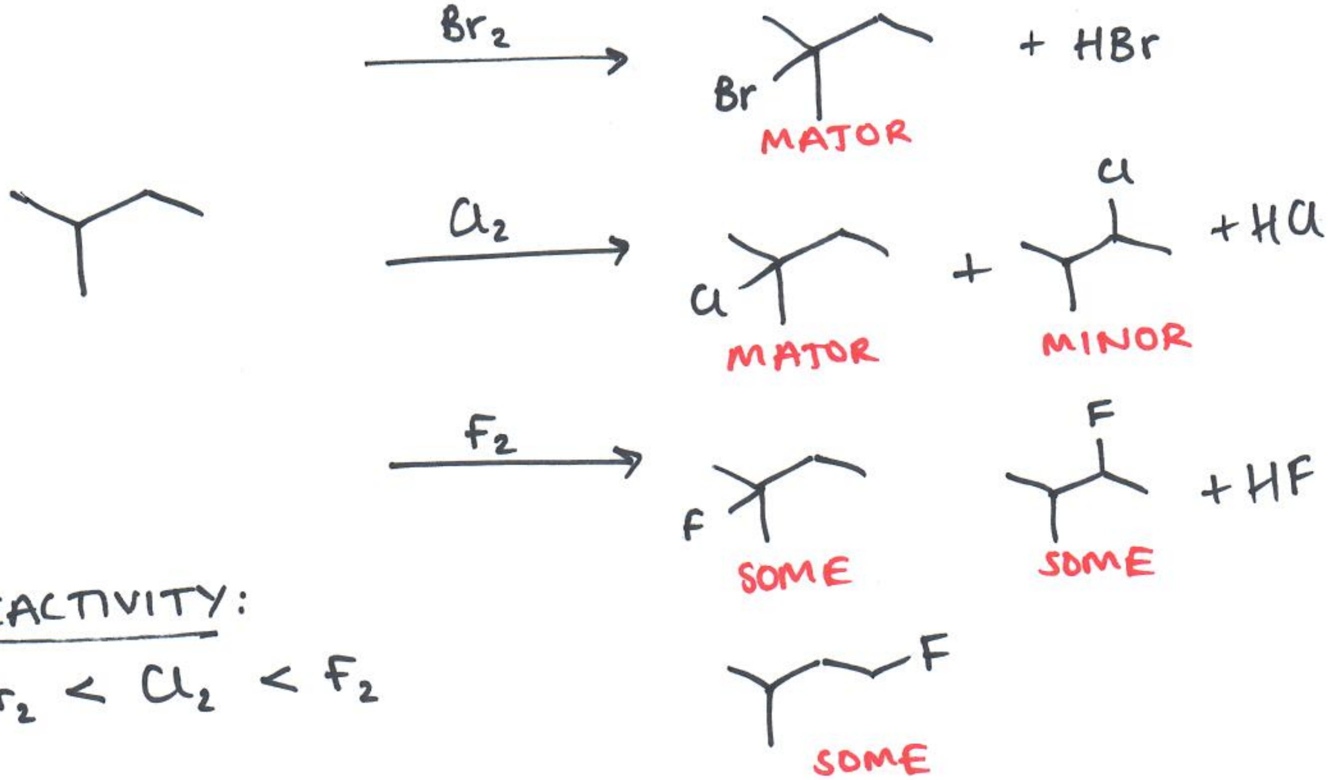




MAJOR PRODUCT



MAJOR PRODUCT.

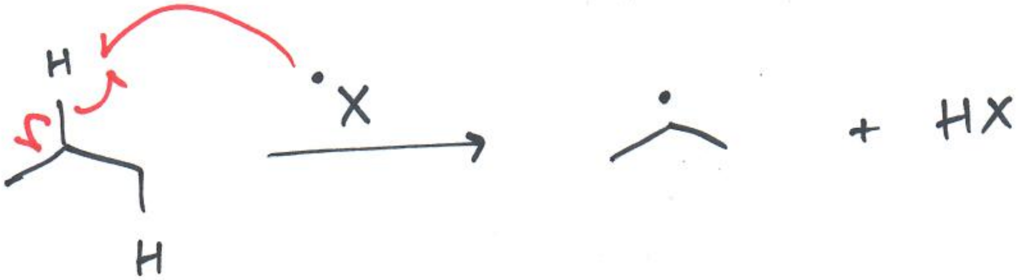


REACTIVITY:

$Br_2 < Cl_2 < F_2$

More reactive halogen ⟹ Less selective reaction

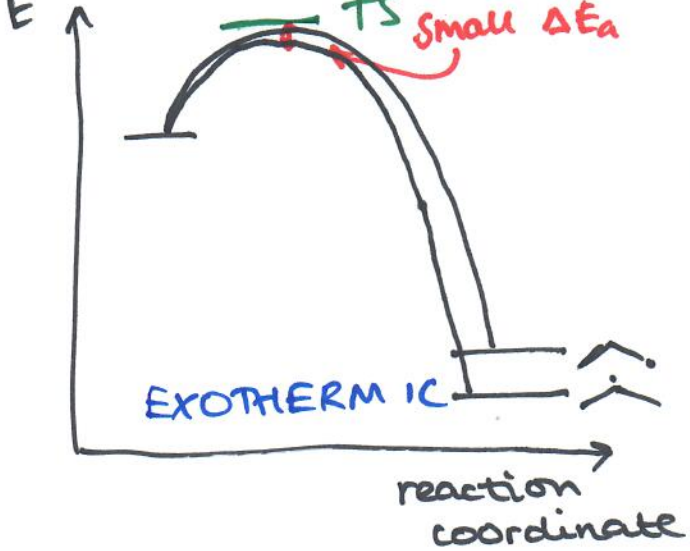
Less reactive halogen ⟹ More selective reaction



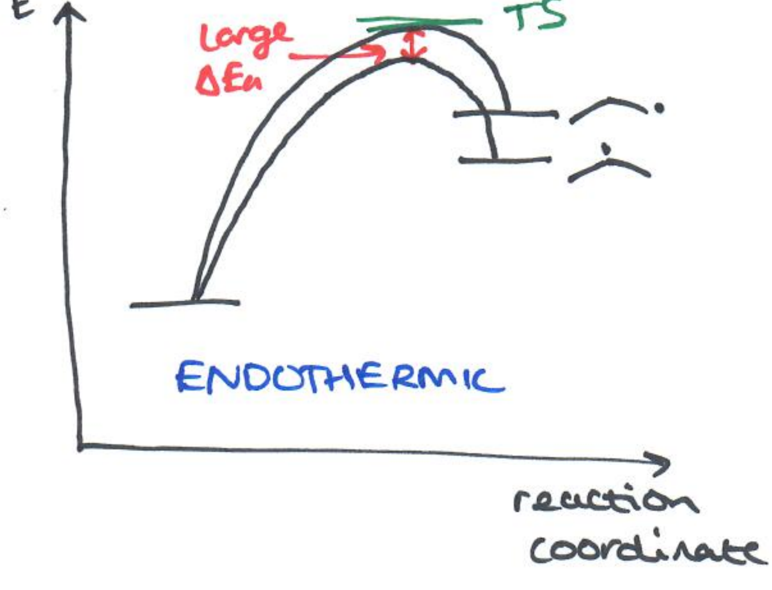
Chlorination => RDS is exothermic => strong HCl bond

Bromination => RDS is endothermic => weaker HBr bond

CHLORINATION



BROMINATION



Early TS - looks more like reactants ↖

Less selective

Small difference in Ea

HAMMOND'S POSTULATE

↗ Late TS - looks more like products.

More selective

Larger difference in Ea.