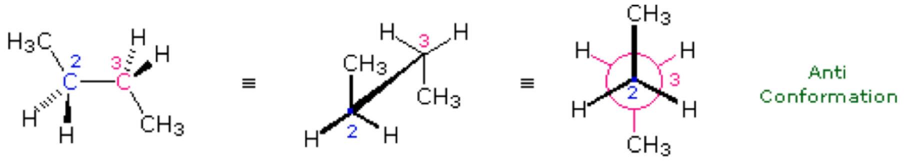
Recall: A molecular <u>conformation</u> is any spatial arrangement of atoms that can be interconverted by rotation about single bonds of the molecule.

Rotation around all bonds still very rapid.
Most stable (most populated conformation) is called anti and has groups as far away as possible.
Note: Newman Projection allows you to look at only one bond at a time. In the case of n-butane, we are looking through the central bond.

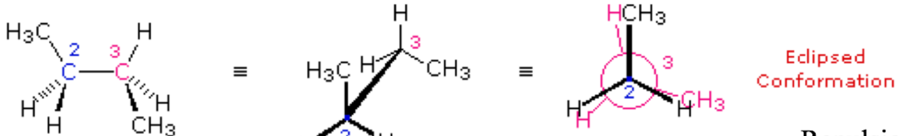
A



Most stable, staggered

Dihedral angle = 180°

B

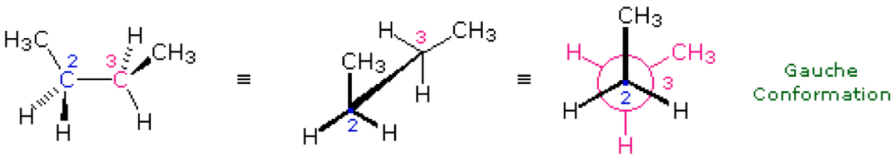


Dihedral angle = 120°

Repulsion = steric effect

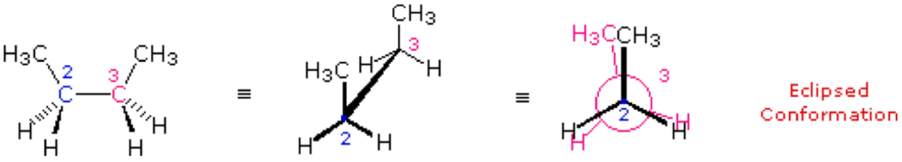
Not as stable as anti

C



Dihedral angle = 60°

D

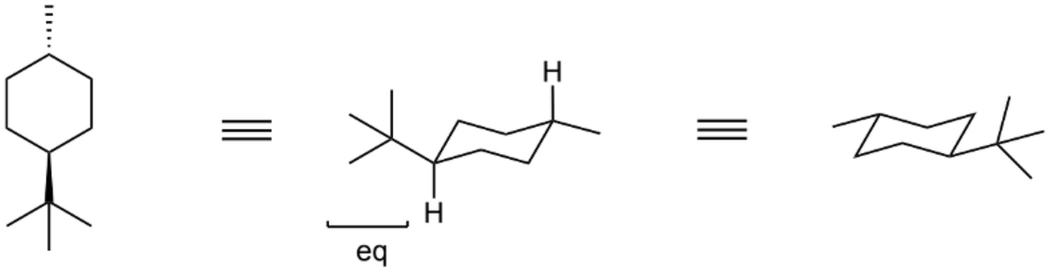


Least stable (syn) eclipsed

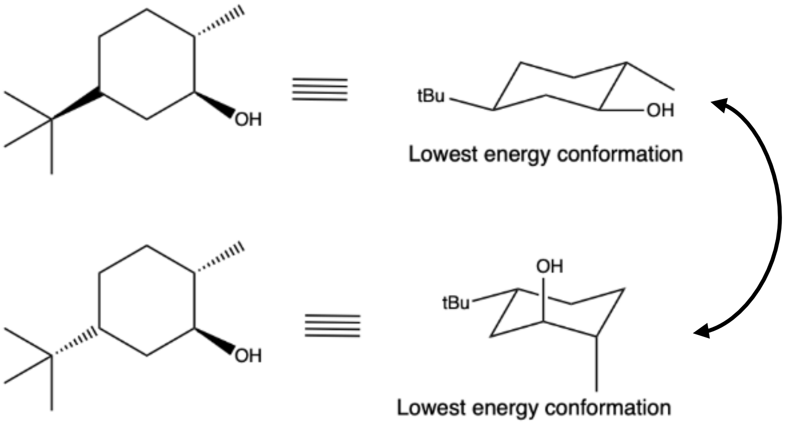
Dihedral angle = 0°

Cyclohexane molecules usually prefer to exist as chair conformations. Steric strain drives the lowest energy conformation.

Ex 1)

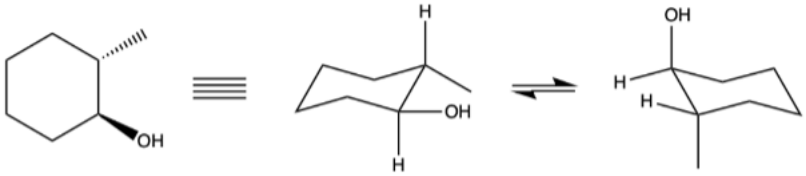


Ex 2)



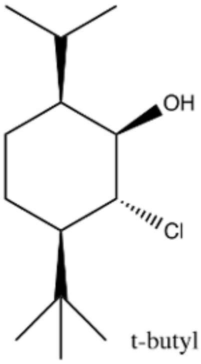
These two structures are stereoisomer of each other

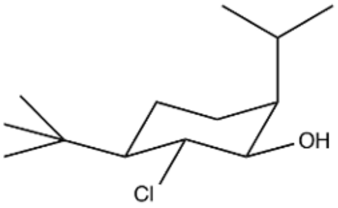
Ex 3)



Lowest energy conformation

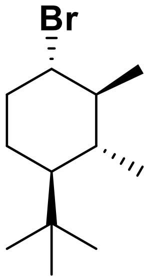
Ex 4)

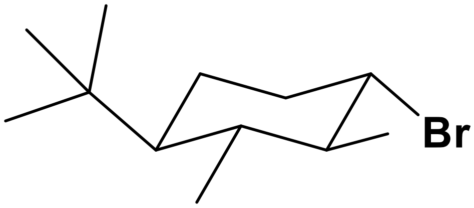




t-butyl is largest --> start by putting it equatorial

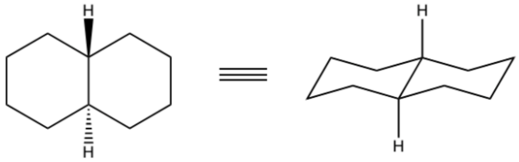
Ex 5)



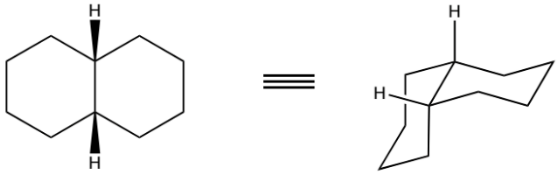


Examples of Basic Bicyclic Compounds:

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

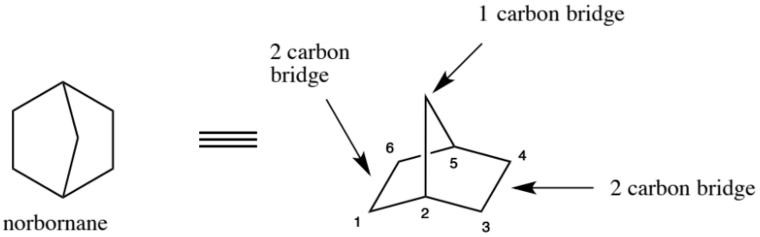


cis-Decalin:



Stereoisomers

2 degrees of unsaturation

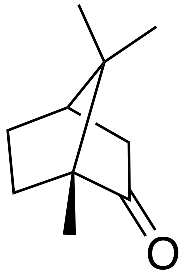


norbornane
C_7H_{12}
Degrees of unsaturation: 2

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

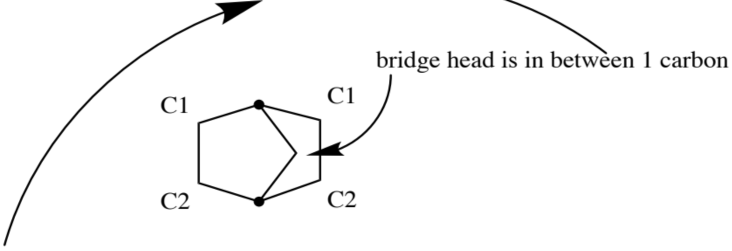
You are not responsible for nomenclature of bridged bicyclic compounds described below, but you should know norbornane and decalin structures above

Examples with norbonane moeity



Camphor

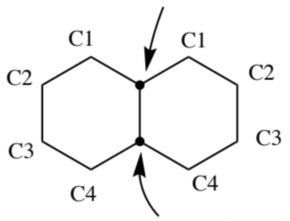
Bicyclic Nomenclature: **2, 2, 1**



bridge head is in between 1 carbon

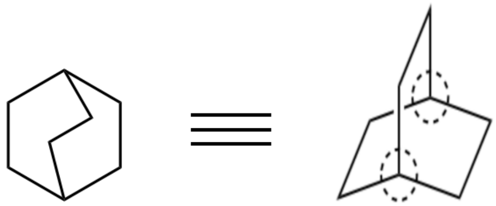
there are two sets of two carbons (C1, C2) on both sides of the bridge head, hence, 2, 2

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



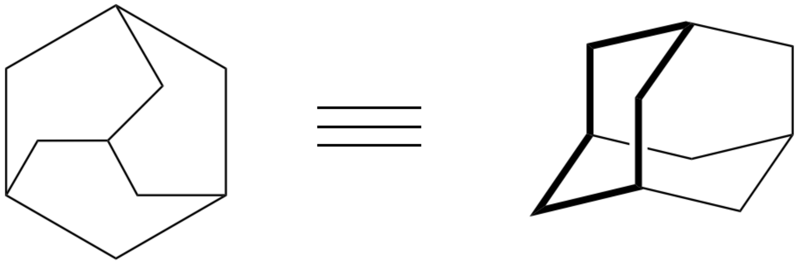
bridge heads in position 0

bridge heads in position 0



2,2,2-Bicyclooctane

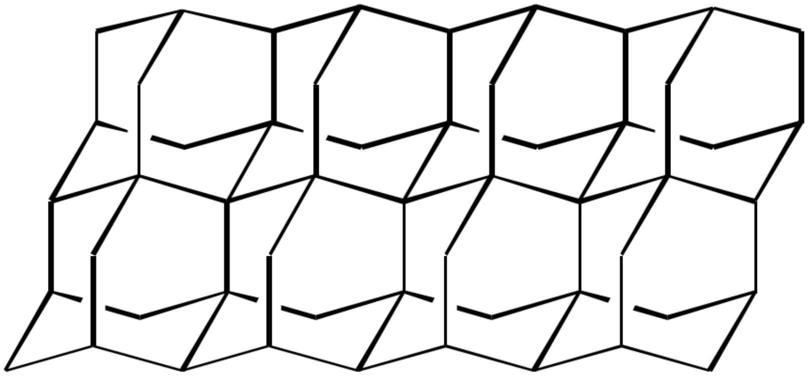
A tricyclic compound:



Adamantane

- This will be the basic structure of diamond

Diamond:



Reactions of alkanes

1) Combustion:

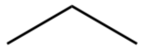
$$R\text{-}H \quad + \quad O_2 \quad \xrightarrow{\Delta=\textbf{heat}} \quad CO_2 \quad + \quad H_2O$$

R = any alkyl group

General formula for combustion reactions:

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

e.g. propane



$CH_3CH_2CH_3$

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

2) Halogenation (Radical substitution reaction)

*****Know these halogens: F, Cl, Br, I → these are diatomic

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

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 $\times 10^{-34}$ joules-sec
ν = frequency of light
E = hν, are the symbols we use to describe light energy

In this course, we will focus on chlorination and bromination.

Substitution reaction (via <u>radicals</u>) – 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

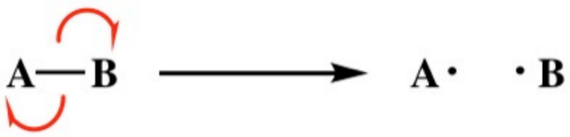
$$CHCl_3 + Cl_2 \xrightarrow{h\upsilon} CCl_4 + HCl$$

carbon tetrachloride
tetrachloromethane

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

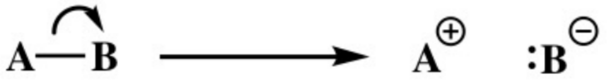
Two kinds of mechanism

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 (single hook arrow) above describe the movement of one electron, full arrows describe movement of lone pairs. These no longer have an inert gas configuration and thus are unstable.

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

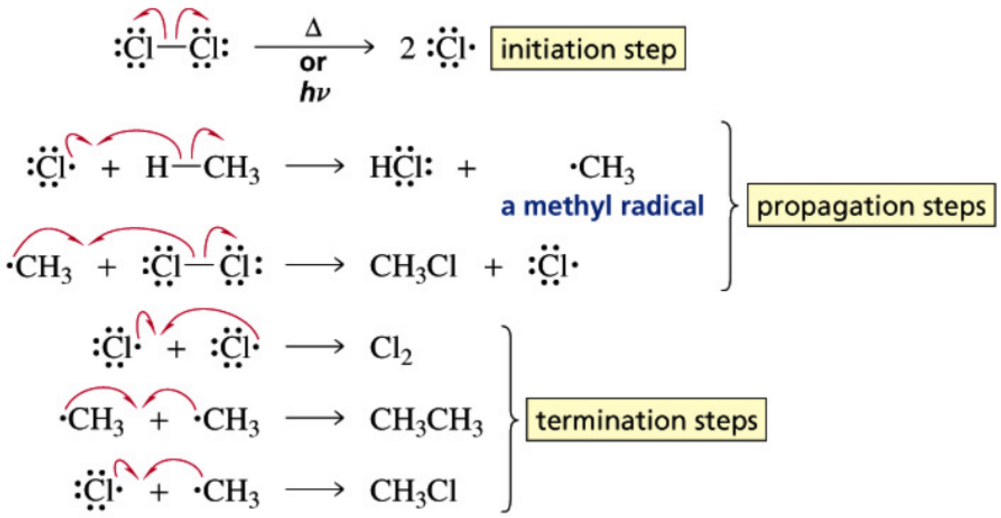


Homolytic reactions are less common than heterolytic reactions

- 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: Methane (analogues)

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

Chloromethane

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

Dichloromethane

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

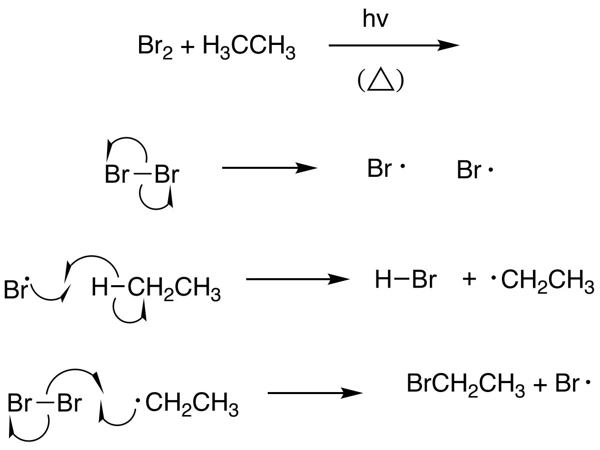
Trichloromethane

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

Tetrachloromethane

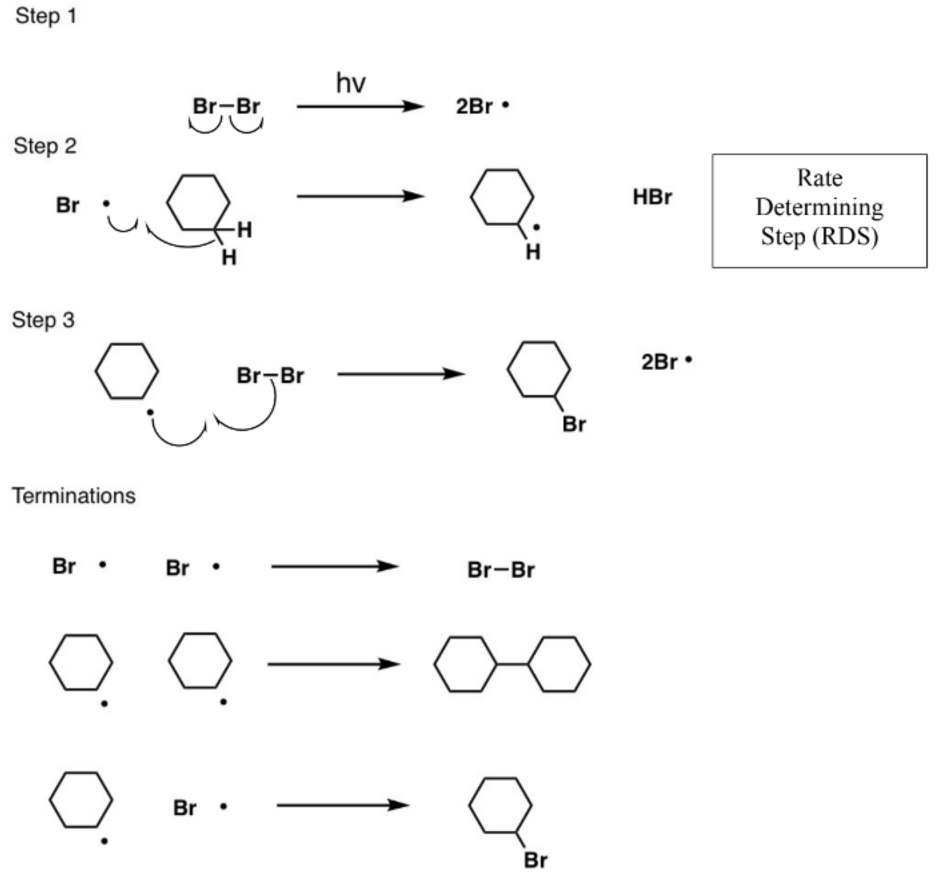
*You should be able to identify if the products have a net dipole

Eg. Bromination of ethane



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)



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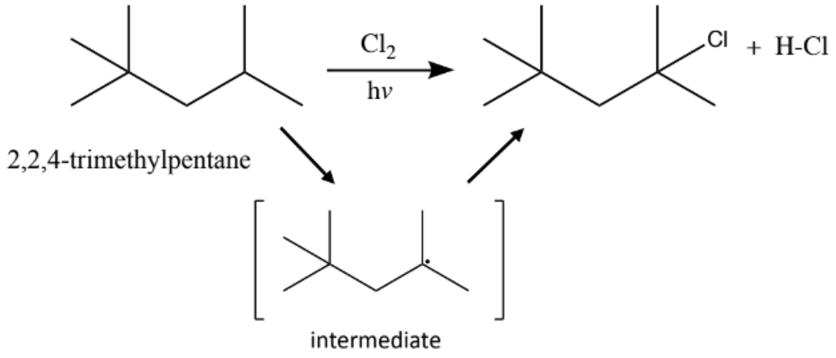
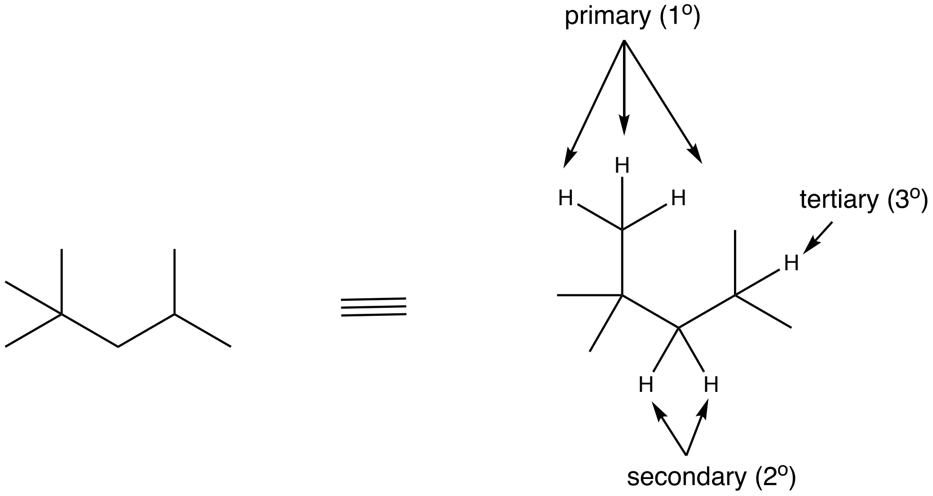
Example: Chlorination of 2,2,4-trimethylpentane

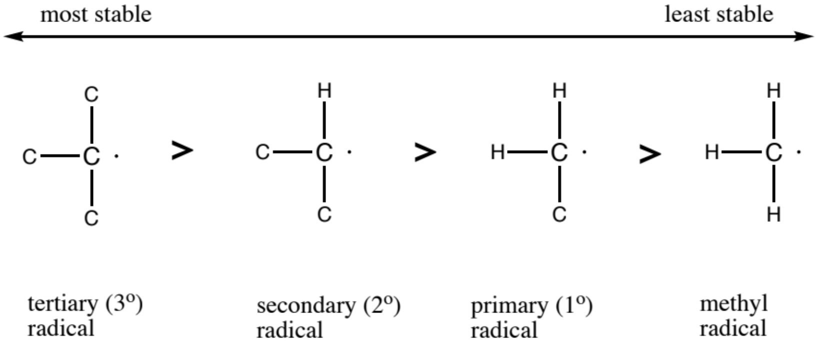


Note: Different types of hydrogen can be pulled from a 2,2,4-trimethylpentane in a radical halogenation reaction to give various products. However, one main product is obtained. This is explained in terms of the stability of the radical formed during the reaction process.



Stability of radicals:

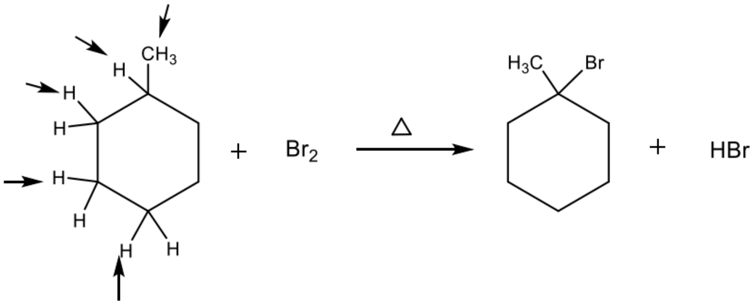
- Stability increases with alkyl substitution
- Alkyl groups are polarizable and donate electrons to electron deficient sites better than hydrogens (this is called **inductive effect** and occurs through sigma bonds)



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)

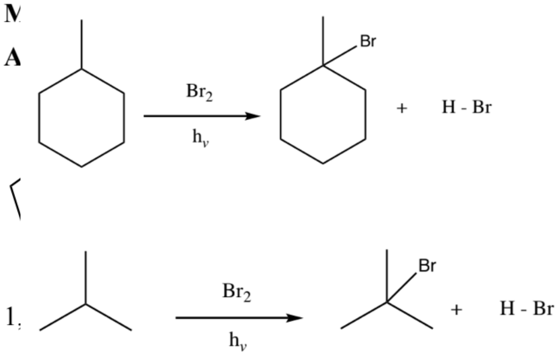
Example: Methylcyclohexane

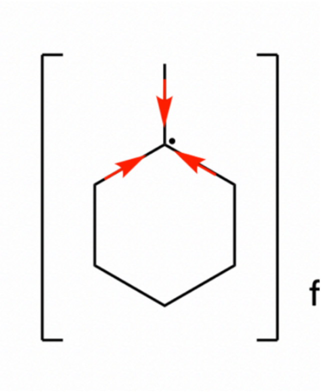


The reaction can utilize either heat (Δ) or light (hν)

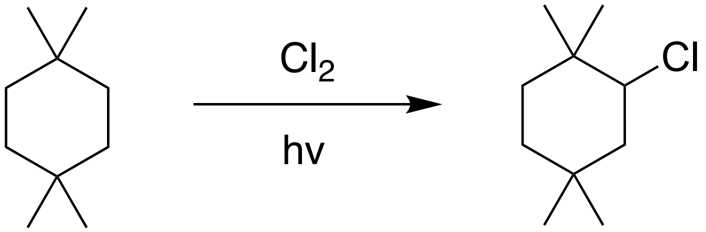
Other Examples:

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

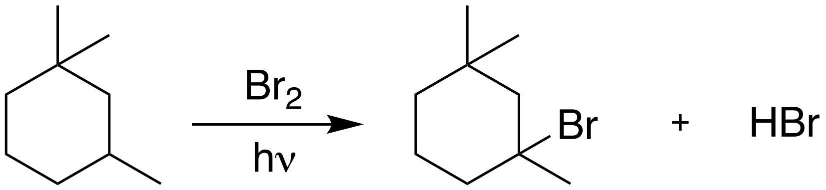




B.

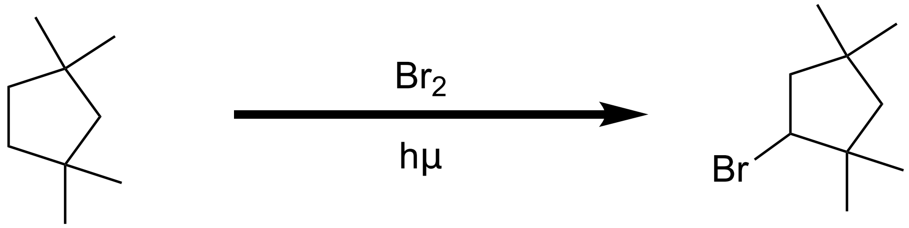


C.



major product

D.

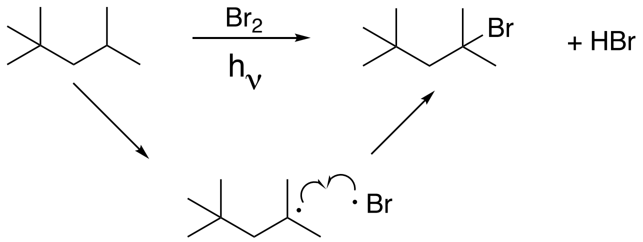


(Sterically favoured product)

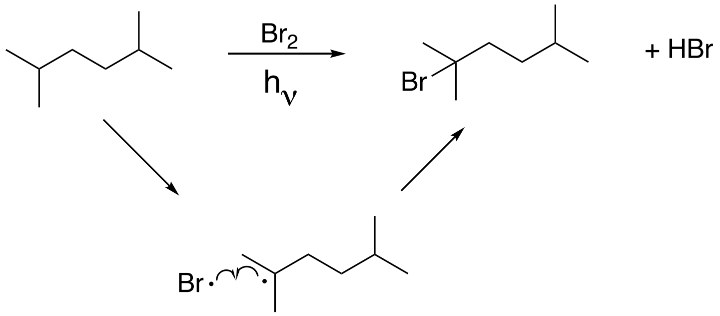
Halogenation reaction mechanisms

Examples:

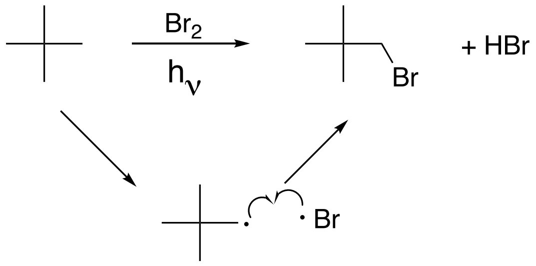
1)



2)

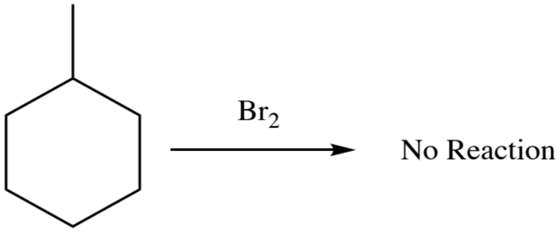


3)

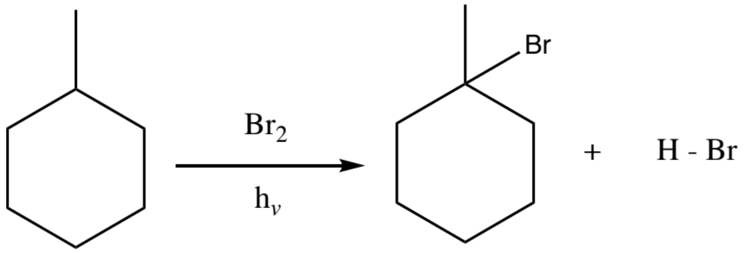


4)

Example:

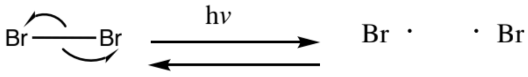


- requires light or heat to cause a reaction between the starting material and halogen.

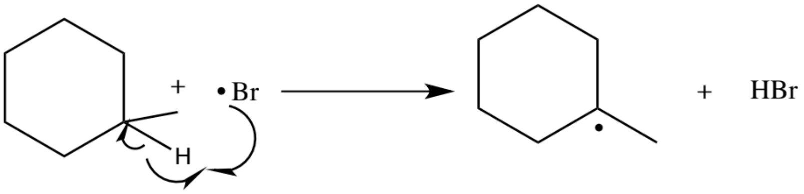


C_7H_{14}

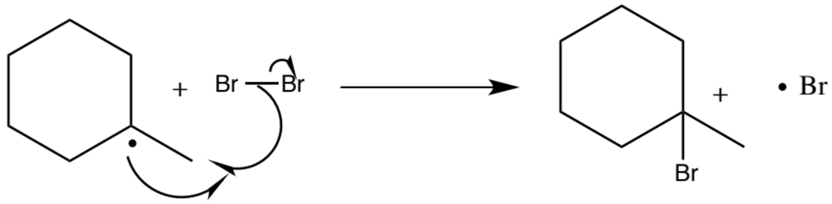
Initiation Step:



Propagation Step 1



Propagation Step 2

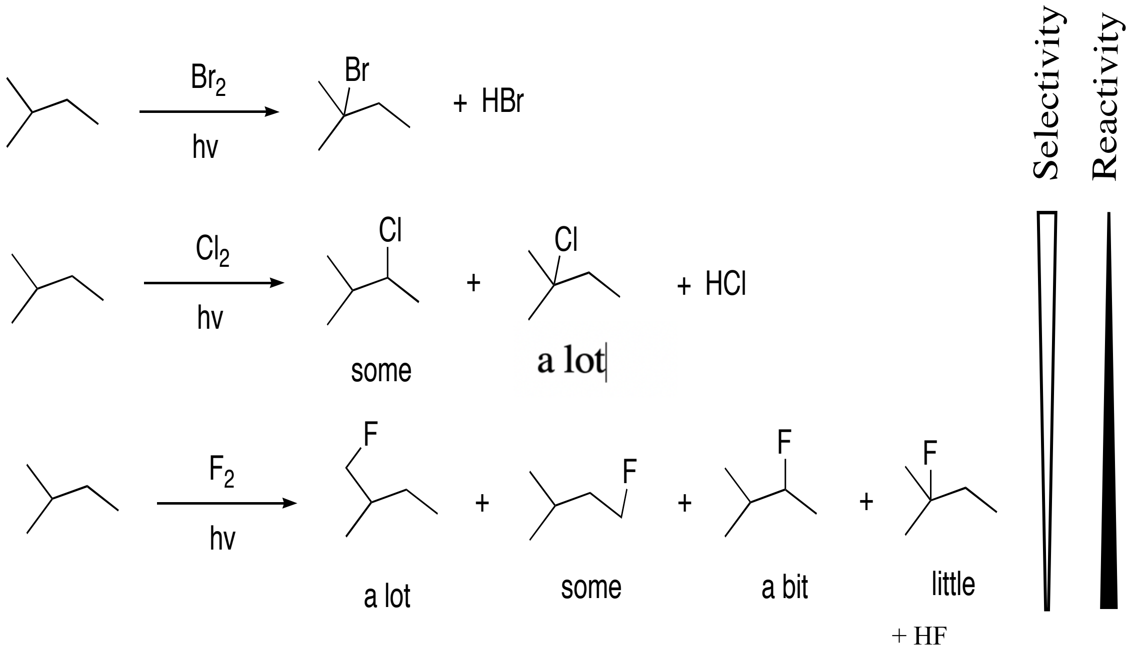


The Hammond Postulate

$R{-}H + X_2 \rightarrow R{-}X + XH$
Reactivity: $F_2 > Cl_2 > Br_2 \gg I_2$ (unreactive)
Selectivity: more reactive → less selective (mixture of products)
Less reactive → more selective (single products)
Hammond's postulate:
Chlorination → RDS is exothermic → early TS → small ΔEa
Bromination → RDS is endothermic → late TS → large ΔEa

Reactivity and Selectivity (Hammond Postulate)

e.g. Halogenation of 2-methylbutane



I_2 does not react as above

The F-radical is highly reactive (highly electronegative) and is the least selective. Typically pulls the first H that it encounters.

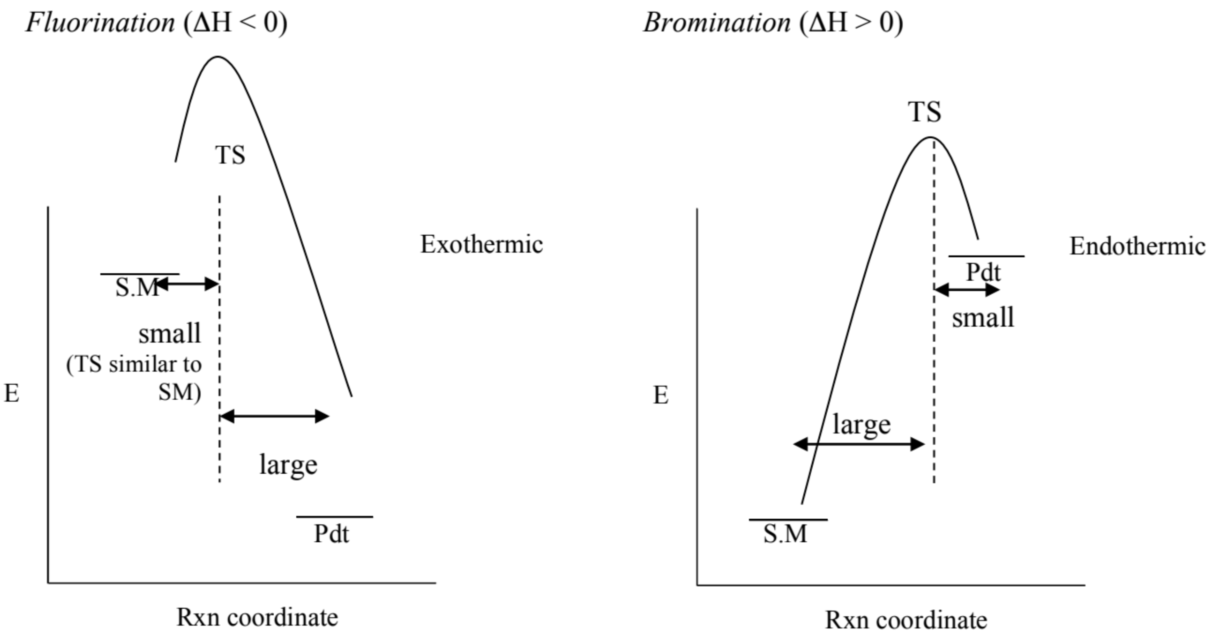
Energy Diagrams of Halogenation Reactions

Note:

Exothermic T.S. (transition state) resembles S.M. (starting material)
Less selective reaction because of a small difference in Ea

Endothermic T.S. resembles product
More selective because of a larger difference in Ea

Energy Diagrams for Halogenation Reactions



E = energy
TS = transition state
SM = starting material

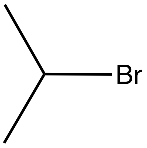
Naming of Alkyl Halides = Haloalkanes

CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Methyl chloride	Methylene chloride	Chloroform	Carbon tetrachloride
Chloromethane	Dichloromethane	Trichloromethane	Tetrachloromethane

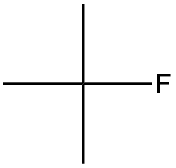
Structure and Nomenclature

1) Find longest chain with largest number of branches
2) Number from end so as to give 1st halogen the lowest number
3) Name prefix with “halo” (chloro, bromo, iodo, fluoro) OR name alkyl and add halide (chloride, bromide, iodide, fluoride) as the suffix

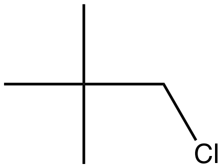
Examples:



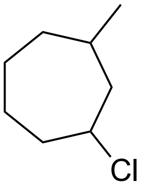
Isopropyl Bromide
2-Bromopropane



tert-Butyl fluoride
2-Fluoro-2-methylpropane



Neopentyl chloride
1-Chloro-2,2-dimethylpropane



1-Chloro-3-methylcycloheptane