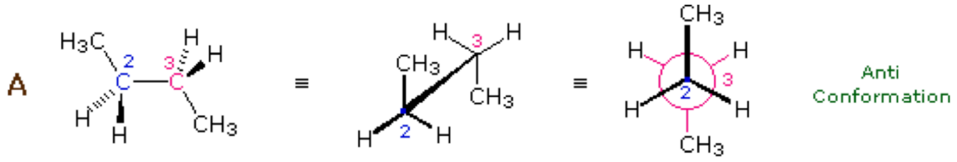
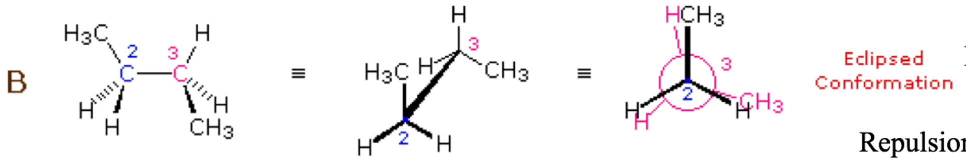
Recall: A molecular conformation is any spatial arrangement of atoms that can be interconverted by rotation about single bonds of the molecule.

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.



Most stable, staggered

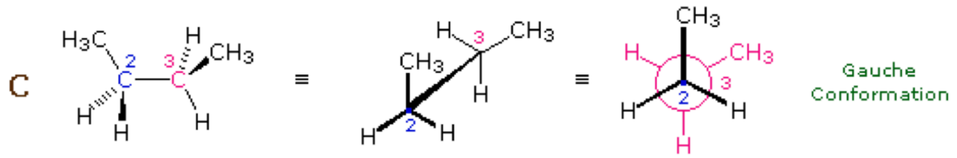
Dihedral angle = 180°



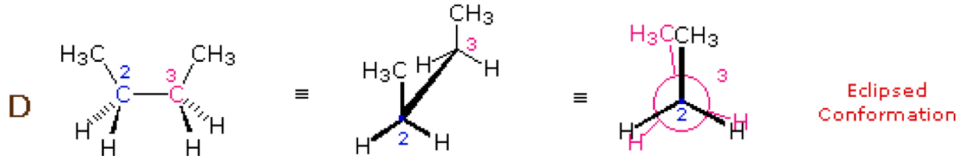
Dihedral angle = 120°

Repulsion = steric effect

Not as stable as anti



Dihedral angle = 60°

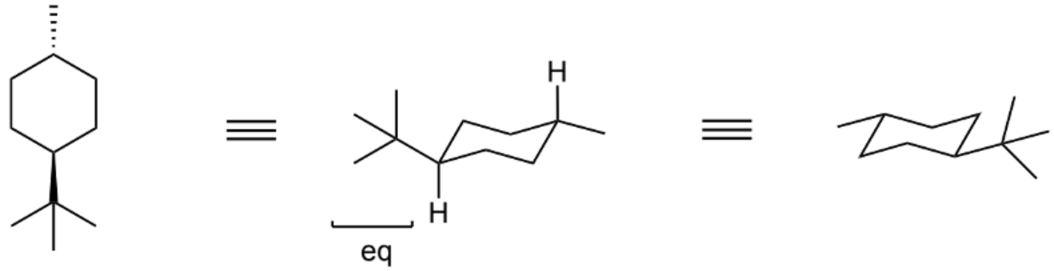


Least stable (syn) eclipsed

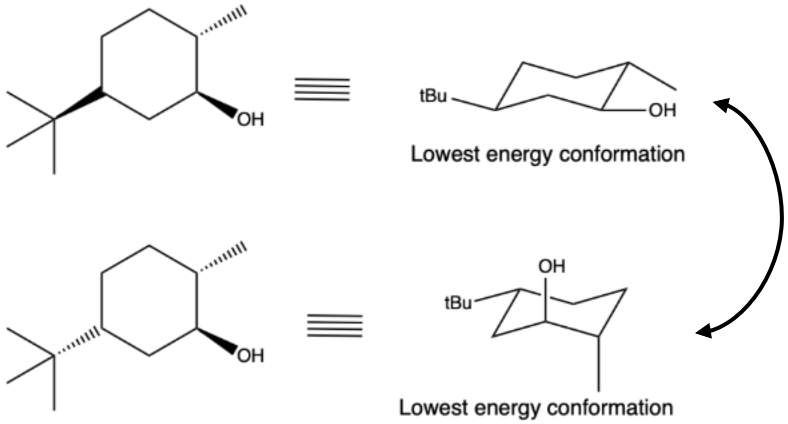
Dihedral angle = 0°

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

Ex 1)

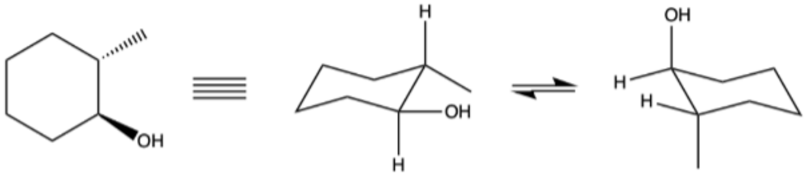


Ex 2)



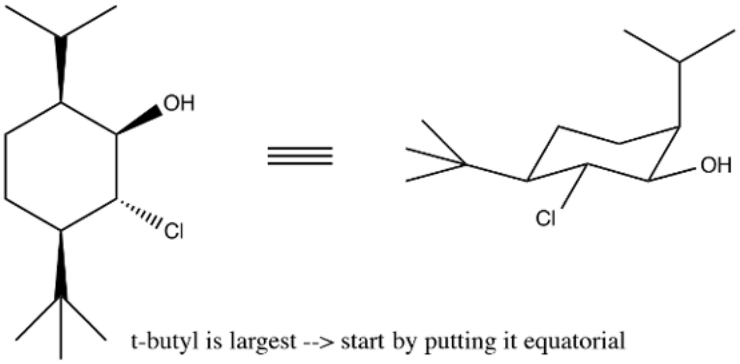
These two structures are stereoisomer of each other

Ex 3)



Lowest energy conformation

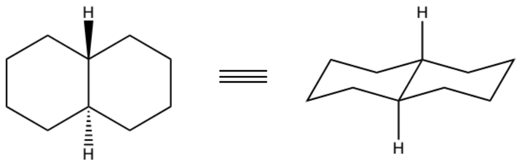
Ex 4)



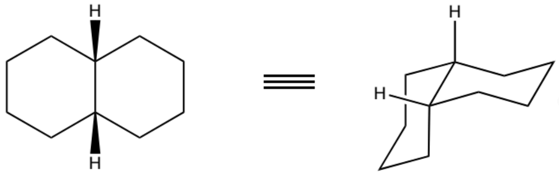
t-butyl is largest --> start by putting it equatorial

Examples of Basic Bicyclic Compounds:

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

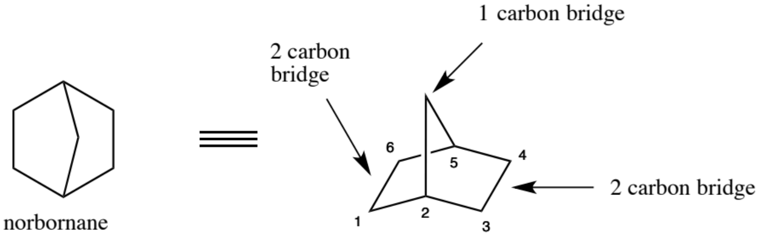


cis-Decalin:



Stereoisomers

2 degrees of unsaturation

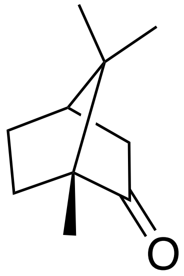


norbornane
C_7H_{12}
Degrees of unsaturation: 2

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

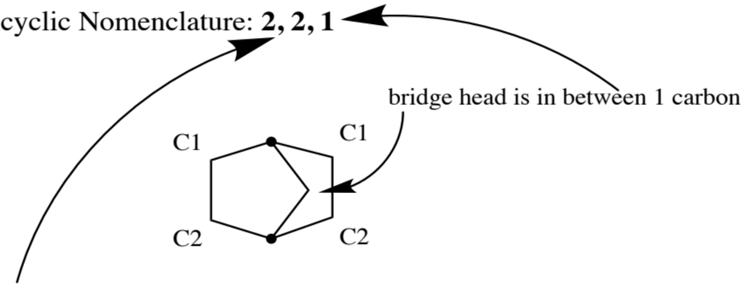
You are not responsible for nomenclature of bridged bicyclic compounds described below, but you should know norbornane and decalin structures above

Examples with norbonane moeity



Camphor

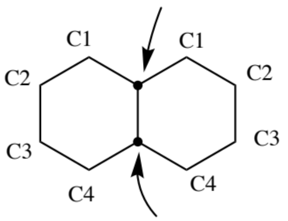
Bicyclic Nomenclature: **2, 2, 1**



bridge head is in between 1 carbon

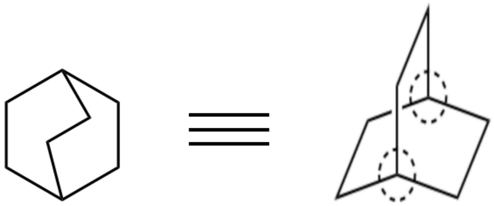
there are two sets of two carbons (C1, C2) on both sides of the bridge head, hence, 2, 2

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



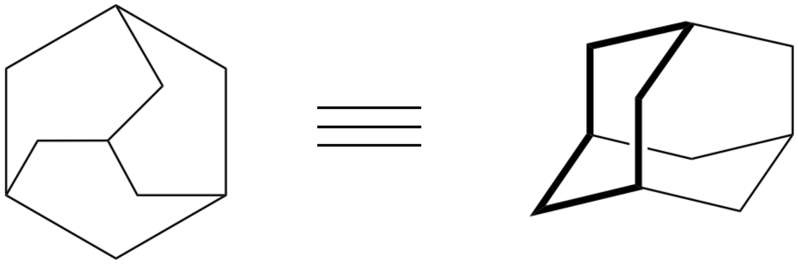
bridge heads in position 0

bridge heads in position 0



2,2,2-Bicyclooctane

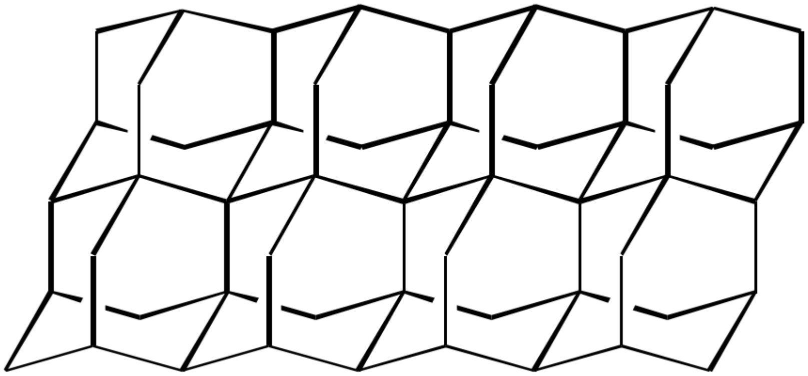
A tricyclic compound:



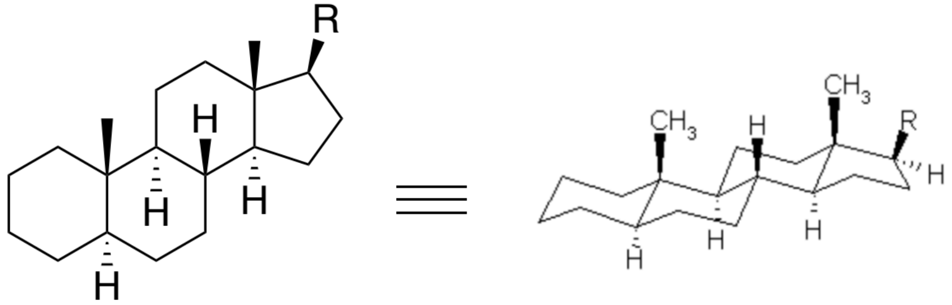
Adamantane

- This will be the basic structure of diamond

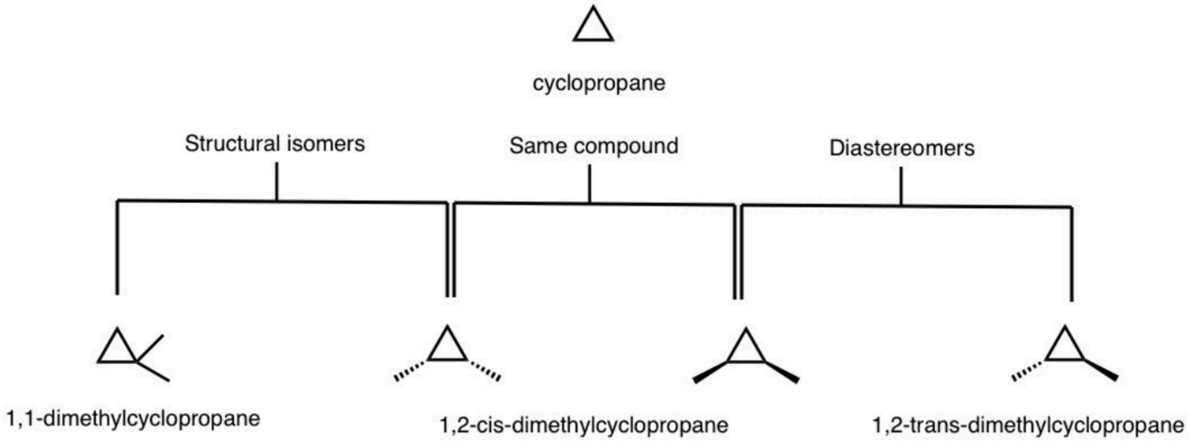
Diamond:



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:

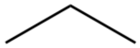
$$\text{R-H} \quad + \quad O_2 \quad \xrightarrow{\Delta=\textbf{heat}} \quad CO_2 \quad + \quad H_2O$$

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



$CH_3CH_2CH_3$

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

2) Halogenation (Radical substitution reaction)

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

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

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 6.6×10^{-34} joules-sec
ν = frequency of light
$E = h\nu$, are the symbols we use to describe light energy

In this course, we will focus 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

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

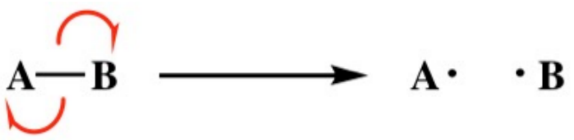
carbon tetrachloride, tetrachloromethane

Mechanism of reaction:

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

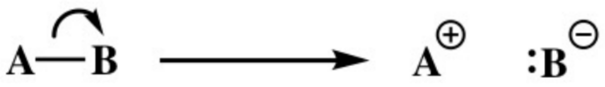
Two kinds of mechanism

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 (single hook arrow) 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

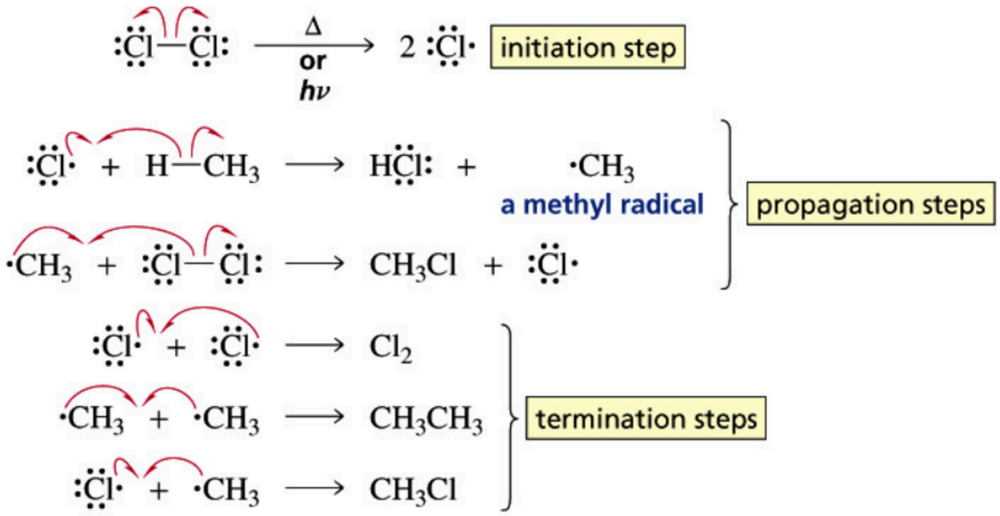


Homolytic reactions are less common than heterolytic reactions

- 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: 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

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

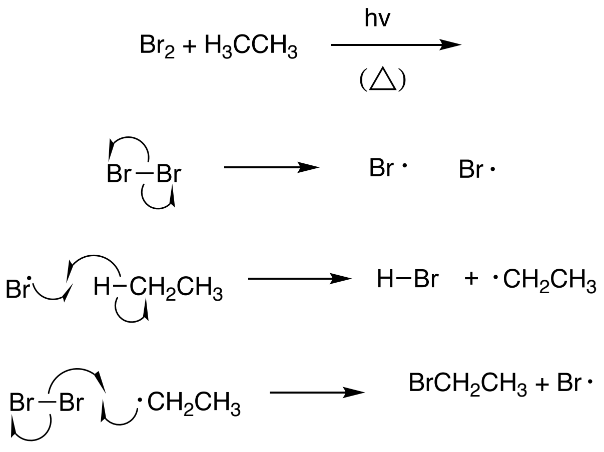
Trichloromethane

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

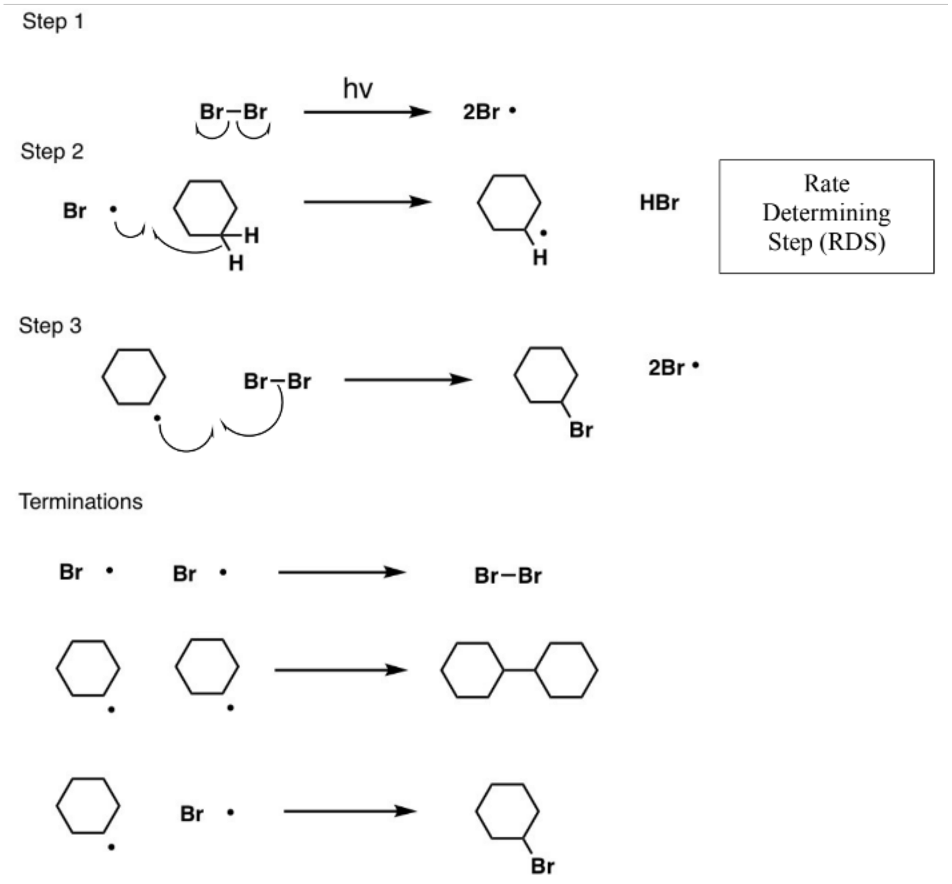
Tetrachloromethane

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

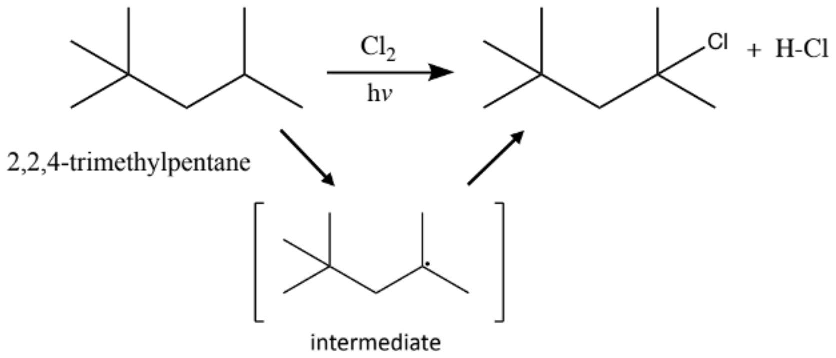
Eg. Bromination of ethane



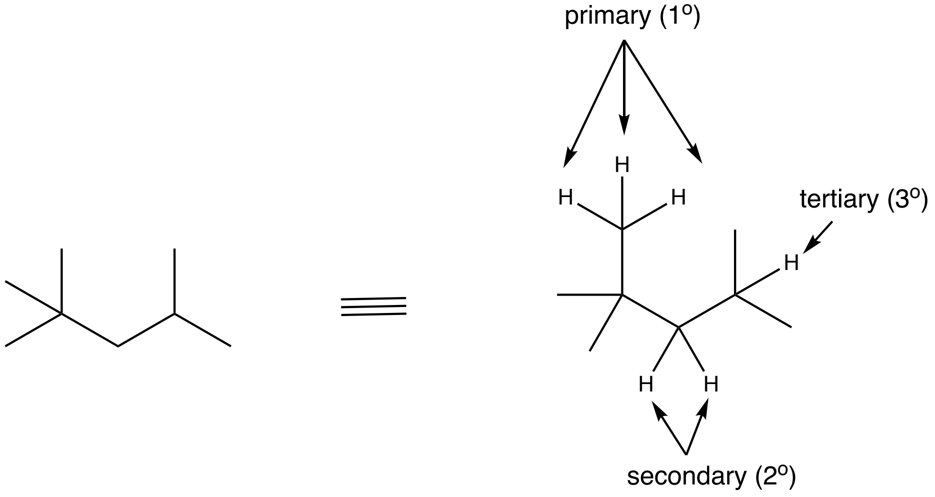
Example: **Bromination of cyclohexane**
(Step 1 is **initiation**, steps 2 and 3 are **propagation** steps that are the main process. Other steps are **termination** steps that shut down the reaction)



Example: Chlorination of 2,2,4-trimethylpentane

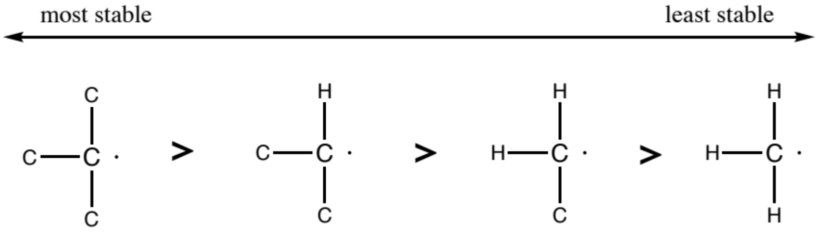


Note: Different types of hydrogen can be pulled from a 2,2,4-trimethylpentane in a radical halogenation reaction to give various products. However, one main product is obtained. This is explained in terms of the stability of the radical formed during the reaction process.



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)

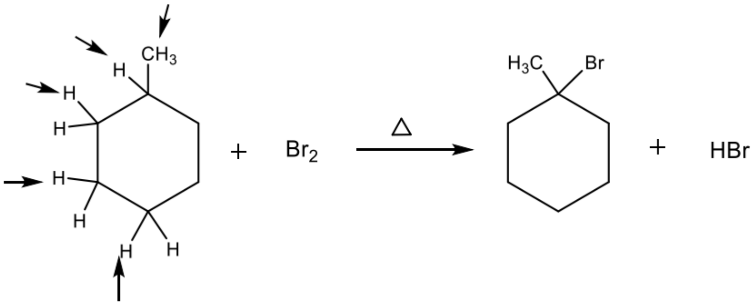


tertiary (3°) radical | secondary (2°) radical | primary (1°) radical | methyl radical

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)

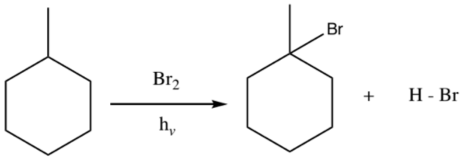
Example: Methylcyclohexane

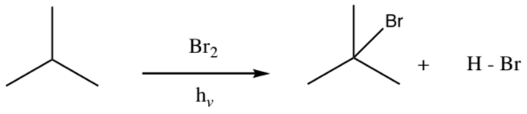


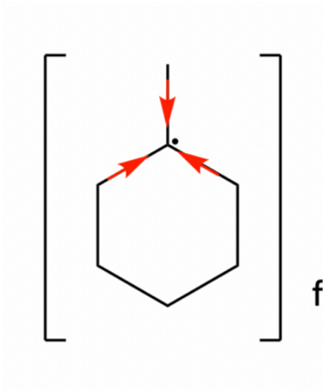
The reaction can utilize either heat (Δ) or light (hν)

Other Examples:

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

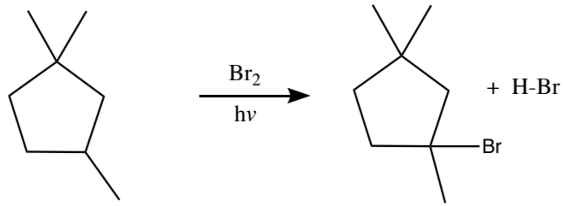






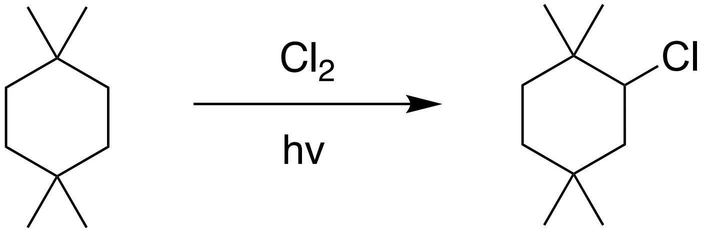
More Examples

A. 1,1,3-trimethylcyclopentane bromination

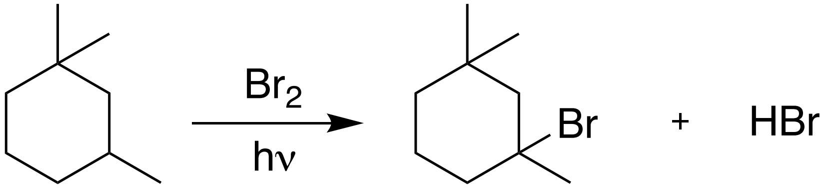


1,1,3-trimethylcyclopentane *(major product)*

B.



C.



major product