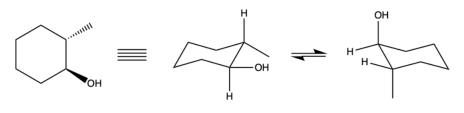
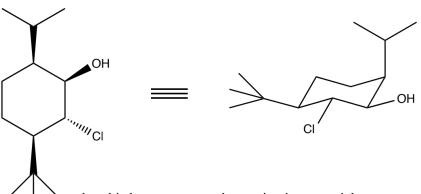
Recall: Cyclohexane molecules usually prefer to exist as chair conformations. Steric strain drives the lowest energy conformation.

<u>Ex1)</u>



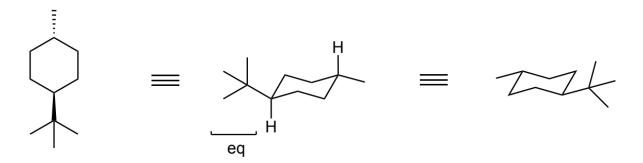
Lowest energy conformation

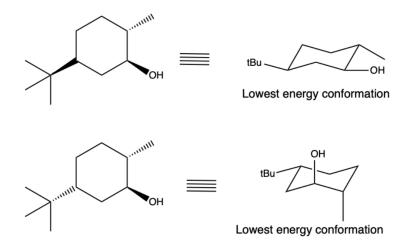
<u>Ex2)</u>



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

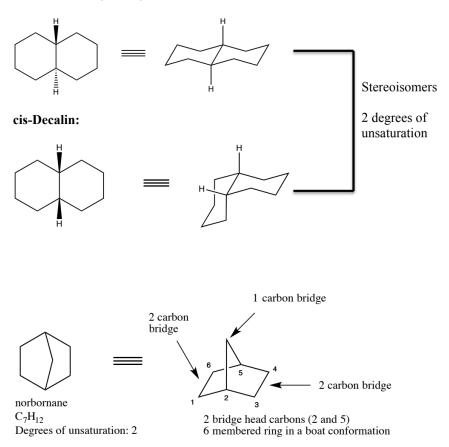
Ex3)



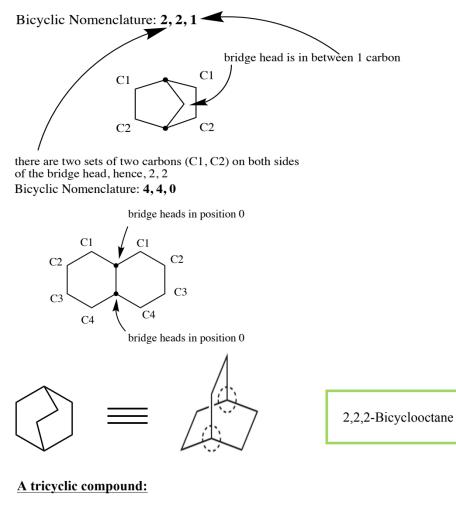


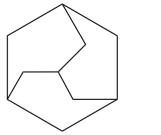
Examples of Basic Bicyclic Compounds:

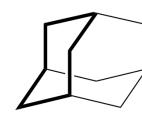
trans-Decalin: (C₁₀H₁₈)



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



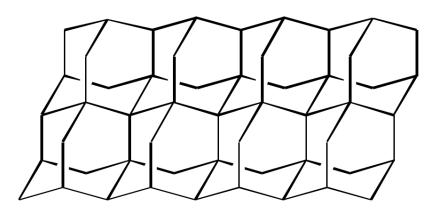




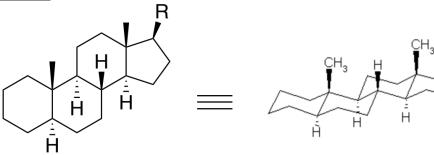
Adamantane

- This will be the basic structure of diamond

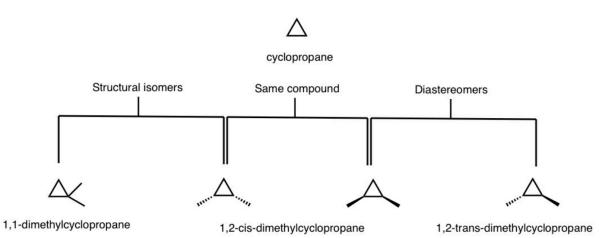
Diamond:



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:

R-H + O_2 \longrightarrow CO_2 + H_2O

R = any alkyl group

General formula for combustion reactions:

$$C_nH_{2n+2} + (\frac{3n}{2} + \frac{1}{2})O_2$$
 (n+1) $H_2O + n CO_2$
e.g. propane

$$\overbrace{CH_3CH_2CH_3}^{\Delta} \qquad \xrightarrow{\Delta} \qquad \qquad 3CO_2 + 4H_2O$$

2) Halogenation

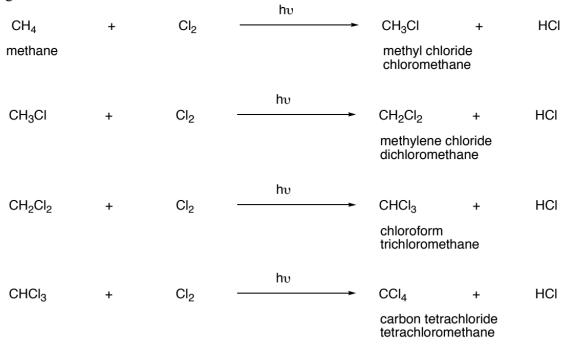
*Know these halogens: F, Cl, Br, I \rightarrow these are diatomic

 $\begin{array}{rrrr} \textbf{R-H} & + & X_2 & & \textbf{hv} \\ R = any alkyl group, R-X = alkyl halide / haloalkane \\ X = halogen \\ F_2 (most reactive) > Cl_2 > Br_2 >> I_2 (does not react) \\ h = Planck's constant 6.6 x10^{-34} joules-sec \\ v = frequency of light \\ E = hv, are the symbols we use to describe light energy \end{array}$

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

Substitution reaction (via radicals) - Substitute H with X

e.g. Chlorination of methane

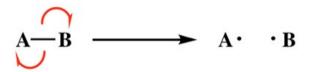


Mechanism of reaction:

- 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 (hu)

Mechanism of halogenation of CH₄:

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)

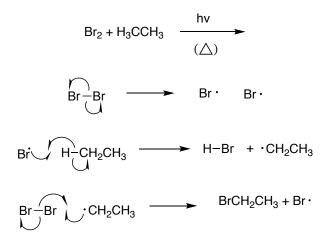
Example: Ethane (analogous)

$$H_3C - CH_3 \xrightarrow{Cl_2} CH_3 - CH_2 - Cl + HCl$$

Example: Methane (analogues)

| CH_4 + | Cl_2 | \xrightarrow{hv} | CH ₃ Cl | + | HCl |
|----------------------|--------|--------------------|--------------------|---|-----|
| | | | Chloromethane | | |
| CH ₃ Cl + | Cl_2 | \xrightarrow{hv} | CH_2Cl_2 | + | HCI |
| | | | Dichloromethane | | |
| $CH_2Cl_2 +$ | Cl_2 | \xrightarrow{hv} | CHCl ₃ | + | HCI |
| | | | Trichloromethane | | |
| CHCl ₃ + | Cl_2 | \xrightarrow{hv} | CCI4 | + | HCI |
| | | | Tetrachloromethane | | |

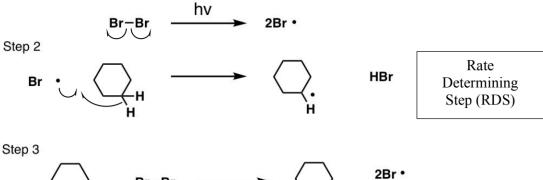
*You should be able to identify if the products have a net dipole **Eg. Bromination of ethane**



Example: Bromination of cyclohexane

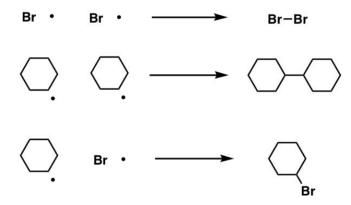
(Step 1 is initiation, steps 2 and 3 are propagation steps that are the main process. Other steps

are **termination** steps that shut down the reaction) Step 1

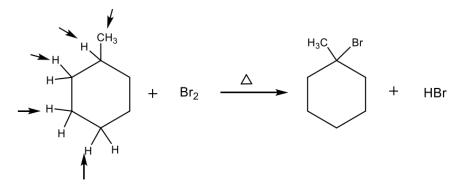


 $\bigcirc Br_Br \longrightarrow \bigcirc Br ^{2B} Br$

Terminations



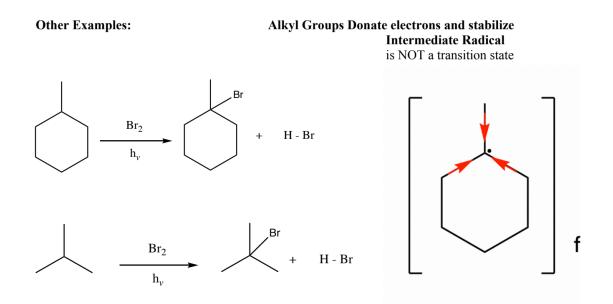
Example: Methylcyclohexane



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

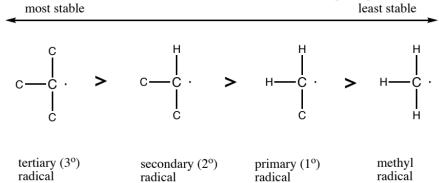
Different types of hydrogen can be pulled from a methylcyclohexane in a radical halogenation reaction to give various products. However, one main product is obtained. This is explained in

terms of the stability of the radical formed during the reaction process.



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)

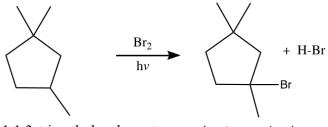


Or it can be summarized from least to most stable radicals:

| ·CH ₃ | < | ·CH ₂ R | < | ·CHR ₂ | < | ·CR ₃ |
|------------------|-----|--------------------|---|-------------------|---|------------------|
| methyl | | primary (1°) | | secondary (2°) | | tertiary (3°) |
| radical | | radical | | radical | | radical |
| (least stab | le) | | | | | (most stable) |

More Examples

A. 1,1,3-trimethylcyclopentane bromination



1,1,3-trimethylcyclopentane (major product)

B. 2,2,4-trimethylpentane chlorination

