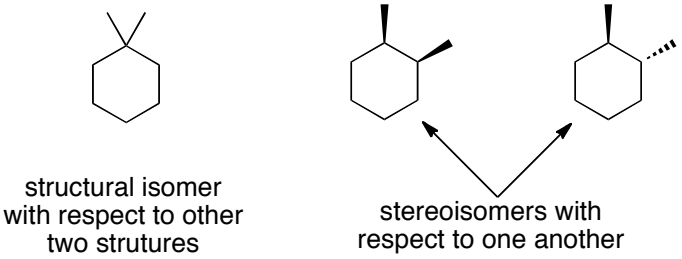
**REVIEW:**

**Conformations** – different shapes a single molecule may assume via rotation around single bonds

**Isomers** - different compounds with same molecular formula – 2 basic types

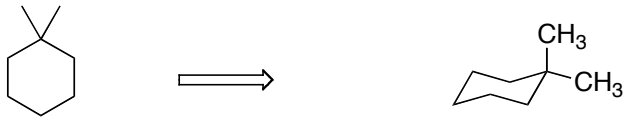
1. Structural/constitutional isomers
   – compounds with same molecular formula
2. Stereoisomers – same connectivity but different 3-D structure – 2 sub-types
   (a) diastereomers/diastereoisomers (eg. *cis*/*trans*)
   (b) enantiomers (non-superposable mirror images of same molecule)

**Example 1**



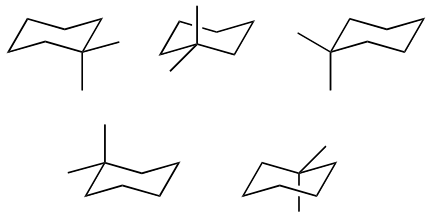
structural isomer with respect to other two strutures

stereoisomers with respect to one another

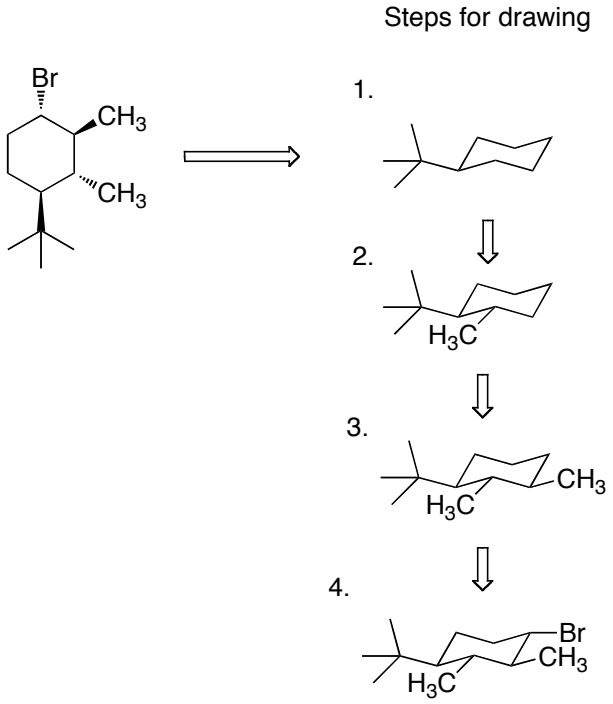



1,1-dimethylcyclohexane

The below are all equally valid representations



**Example 2**




Note on drawing the most stable conformation of substituted cyclohexanes:
- generally, draw chair conformation of cyclohexane
- put the largest group in equatorial position
- draw the next group on the correct side (face) with respect to the largest group

**Reactions of alkanes: two will be considered**

1) **Combustion – already discussed**

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

R=Any alkyl group

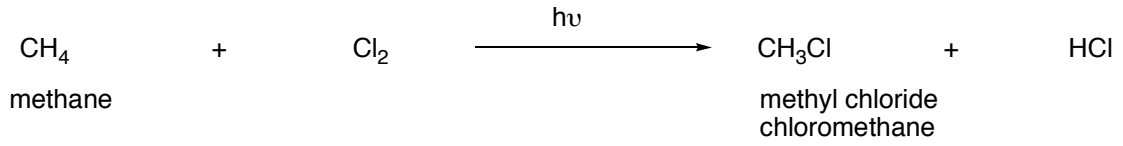
2) **Halogenation of alkanes**

$$R\text{-}H + X_2 \xrightarrow{\text{Light } (h\upsilon)} R\text{-}X + HX$$

R= any alkane (group), R-X = alkyl halide / haloalkane (X=Cl, Br, F) ; $I_2$ fails

substitution reaction – substitute H with X

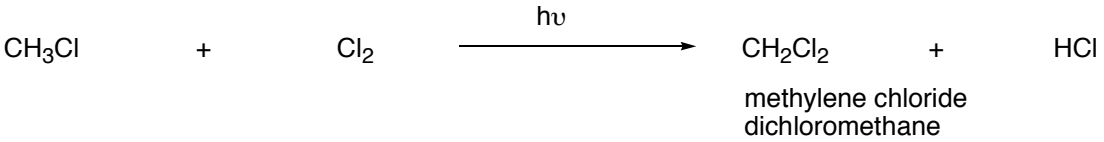
eg.

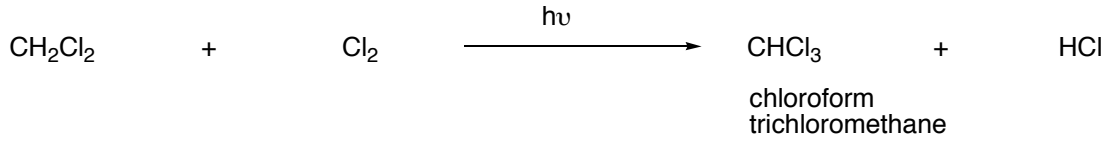


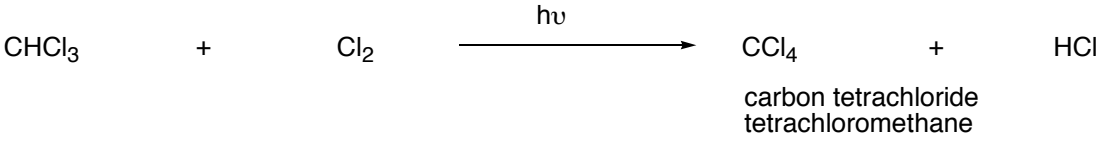

light energy, E = hυ

h = Planck's constant 6.6 x$10^{-34}$ joules-sec

υ = frequency of light



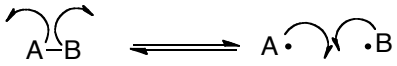




**Mechanism of reaction:**

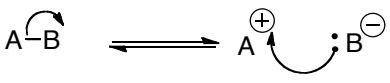
- step by step description of what happens during a reaction (hypothesis)

Two kinds of mechanism-

1. homolytic : (one electron to each atom connected by a bond) radical rxn eg. halogenation of alkanes.




2. heterolytic : (both electrons in bond go to one atom) eg. addition reactions of alkenes, elimination reactions.



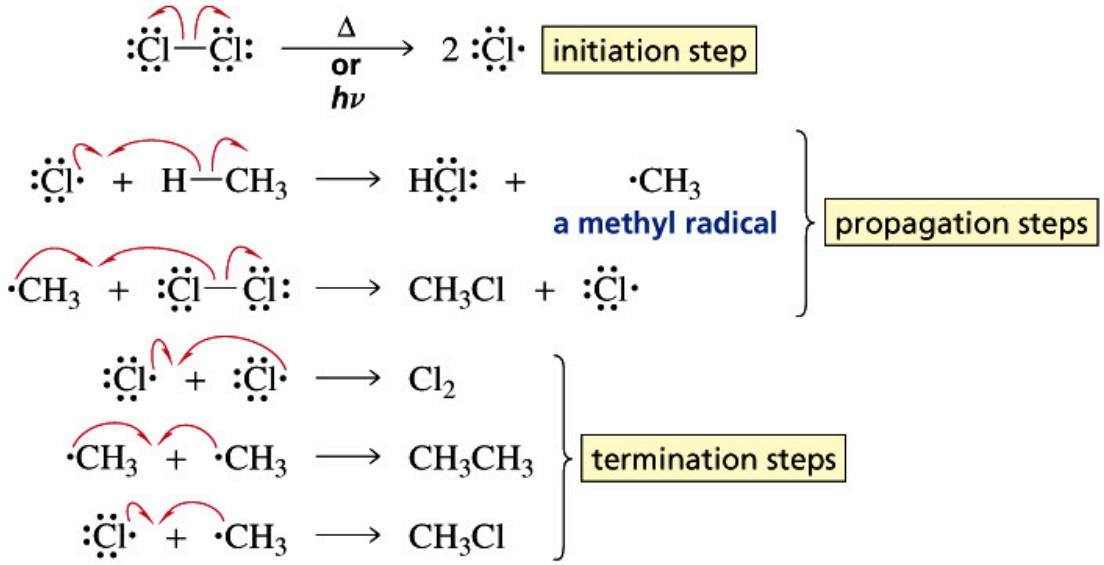

Homolytic reactions (less common than heterolytic reactions)

- initiated by heat (Δ) or by light (hυ)

**Mechanism of halogenation of $CH_4$:**

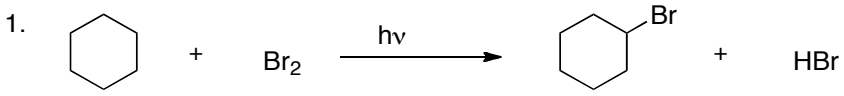
$CH_4 + X_2 \xrightarrow{h\upsilon} CH_3X + HX$

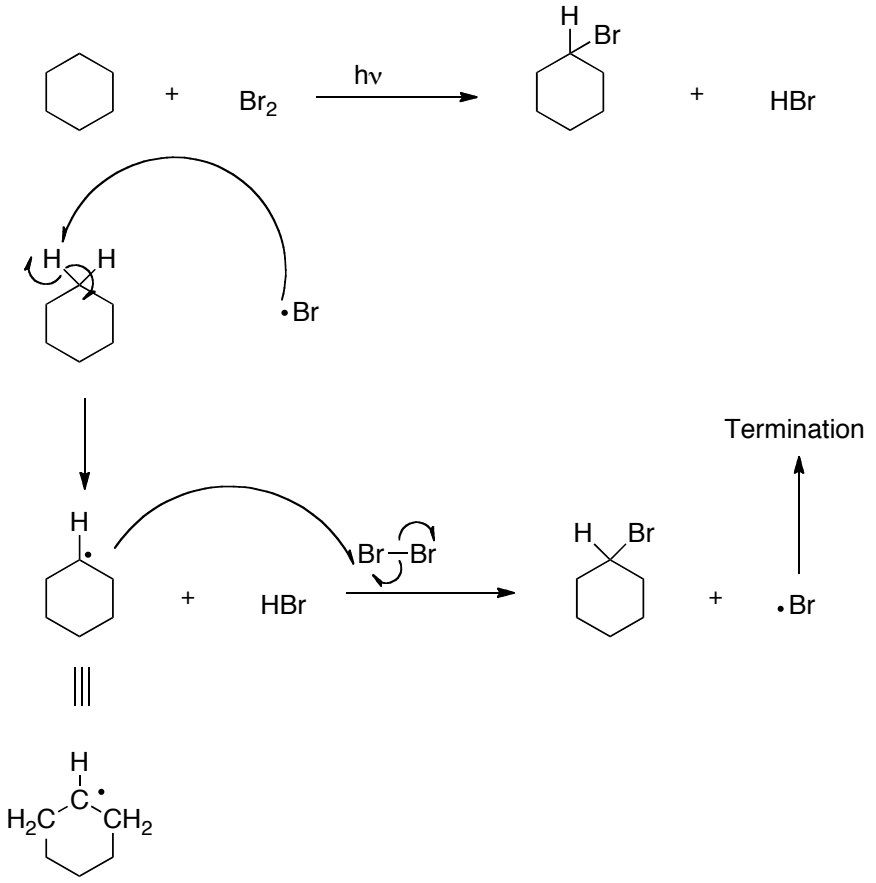
X = F, Cl, Br



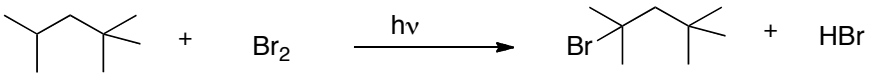

Note: above mechanism applies to other halogens (F, Cl, Br)

Further examples -

1. 




2. "isooctane"



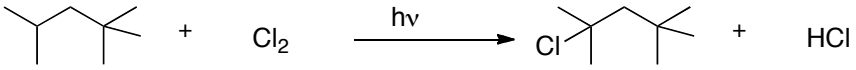

2,2,4-trimethylpentane

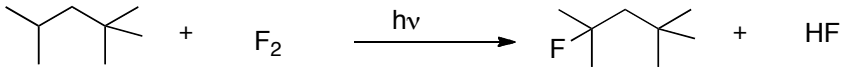
**Stability of radicals:**

Increases with alkyl substitution.
Alkyl groups are polarizable and donate electrons to electron deficient sites better than hydrogens.

| $\cdot CH_3$ | < | $\cdot CH_2R$ | < | $\cdot CHR_2$ | < | $\cdot CR_3$ |
|---|---|---|---|---|---|---|
| methyl radical (least stable) | | primary radical | | secondary radical | | tertiary radical (most stable) |

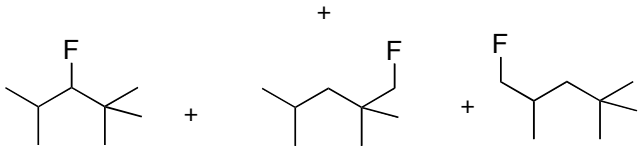
Further Examples

1. 


2. 


minor product

Note: $F_2$ very reactive




major product