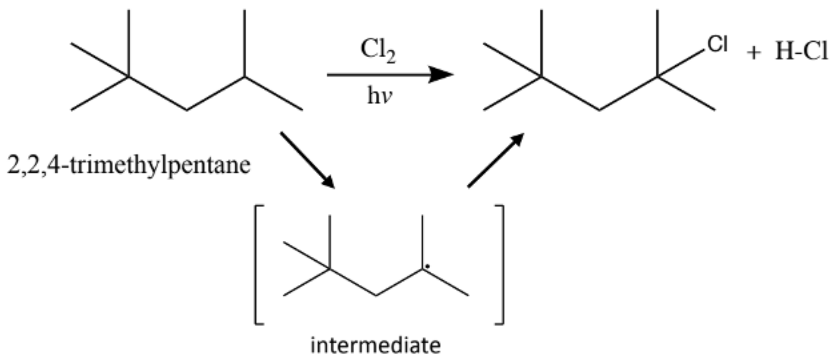
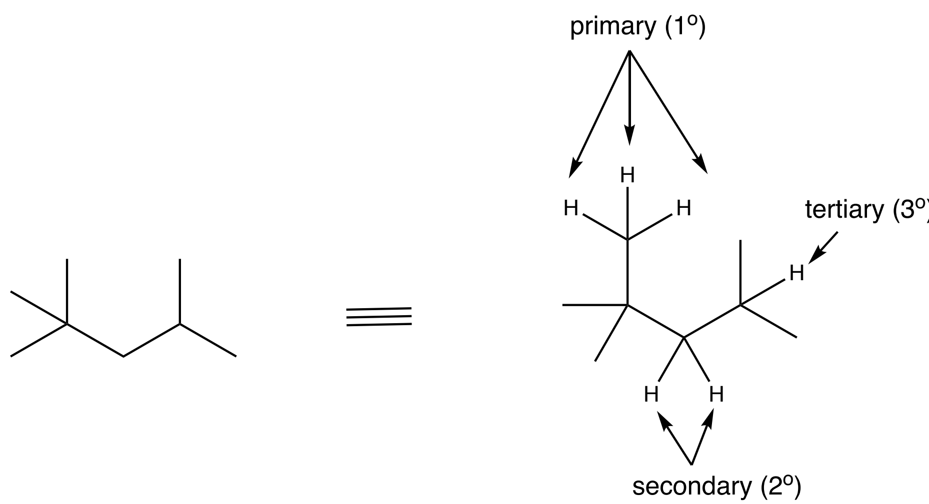
Example: Chlorination of 2,2,4-trimethylpentane



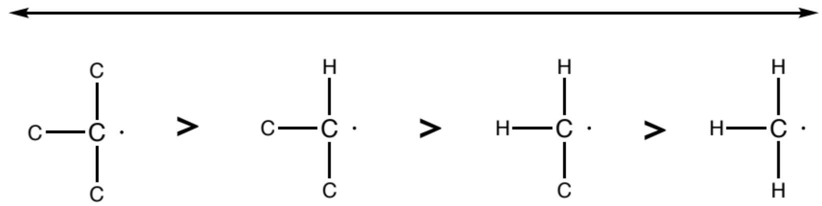
Note: Different types of hydrogen can be pulled from a 2,2,4-trimethylpentane in a radical halogenation reaction to give various products. However, one main product is obtained. This is explained in terms of the stability of the radical formed during the reaction process.



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)

most stable least stable

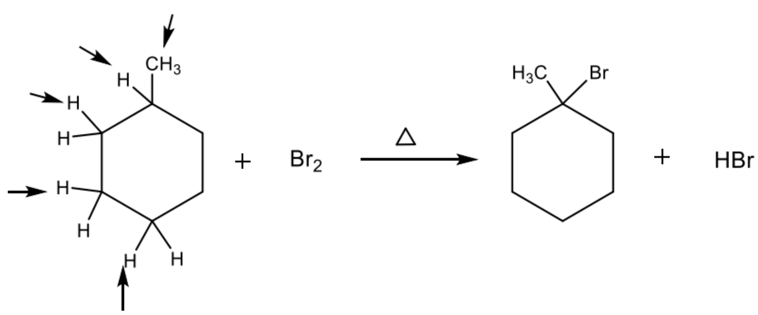


tertiary (3°) radical | secondary (2°) radical | primary (1°) radical | methyl radical

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

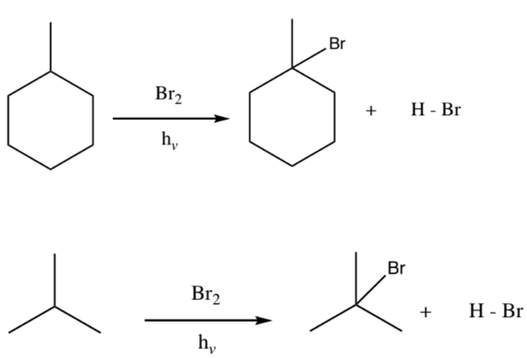
$\cdot CH_3$	<	$\cdot CH_2R$	<	$\cdot CHR_2$	<	$\cdot CR_3$
methyl radical (least stable)		primary (1°) radical		secondary (2°) radical		tertiary (3°) radical (most stable)

Example: Methylcyclohexane

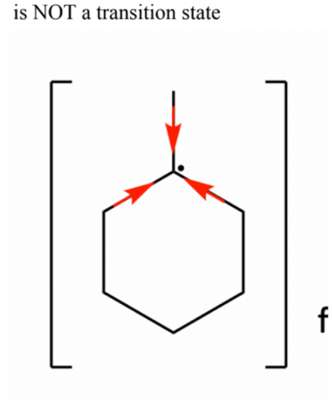


The reaction can utilize either heat (Δ) or light (hν)

Other Examples:

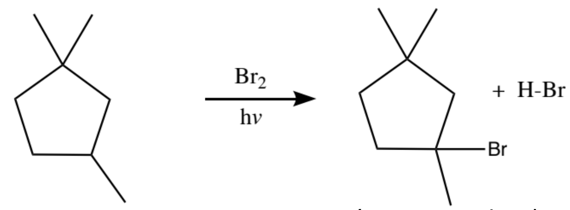


Alkyl Groups Donate electrons and stabilize
Intermediate Radical
is NOT a transition state



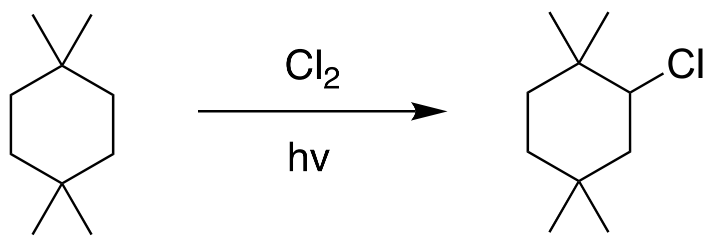
More Examples

A. 1,1,3-trimethylcyclopentane bromination

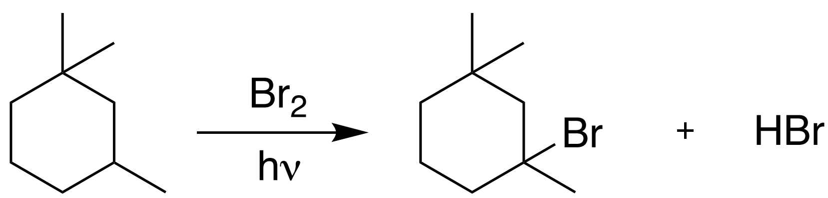


1,1,3-trimethylcyclopentane *(major product)*

B.



C.



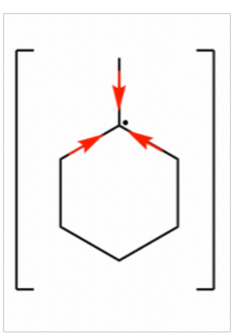
major product

`

Recall:

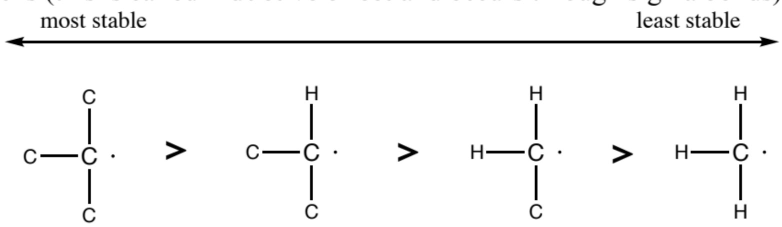
Inductive effect

- Alkyl groups donate (-) charge through the bond and stabilize intermediate radical
- e.g.



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:

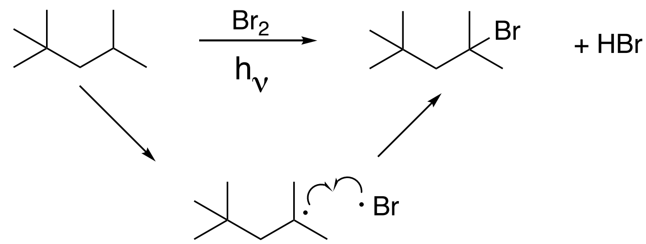
$^{\cdot}CH_3$	<	$^{\cdot}CH_2R$	<	$^{\cdot}CHR_2$	<	$^{\cdot}CR_3$
methyl radical (least stable)		primary (1°) radical		secondary (2°) radical		tertiary (3°) radical (most stable)

Halogenation of alkanes:

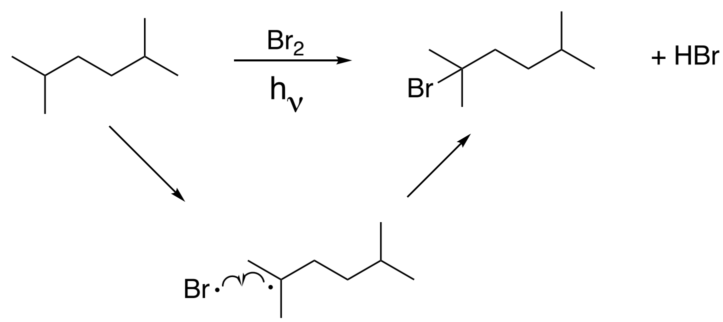
- Requires light or heat to cause a reaction between the starting material and halogen.

Examples:

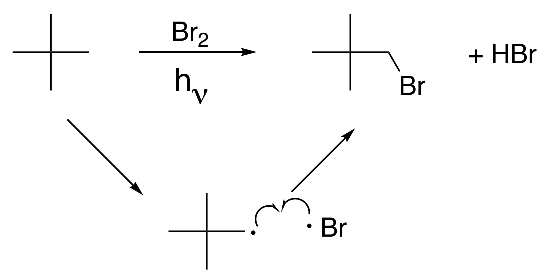
1)



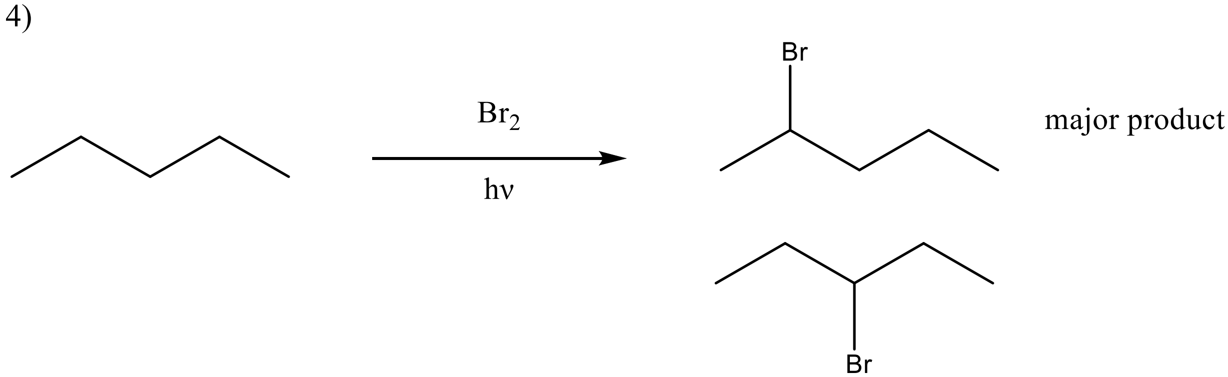
2)



3)

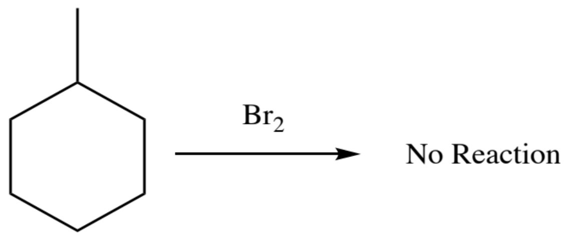


4)

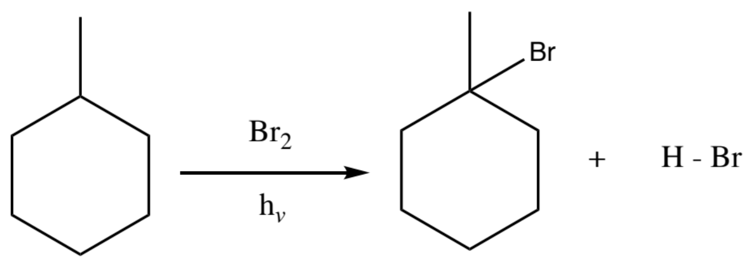


4)

Example:

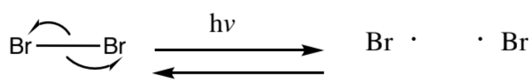


- requires light or heat to cause a reaction between the starting material and halogen.

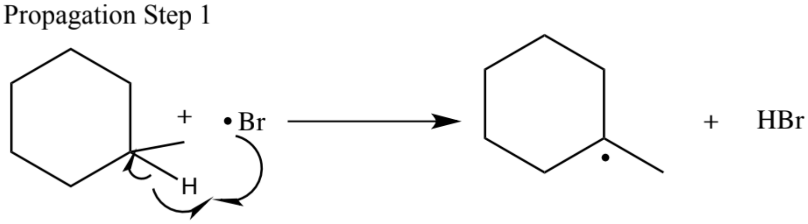


C_7H_{14}

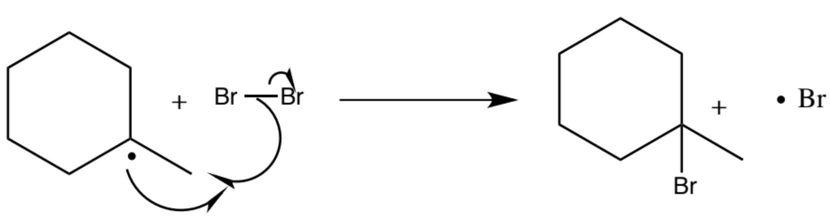
Initiation Step:



Propagation Step 1

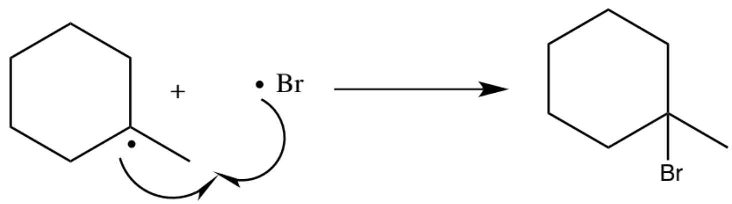


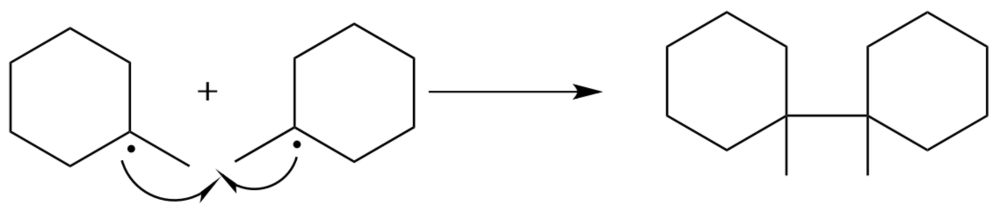
Propagation Step 2



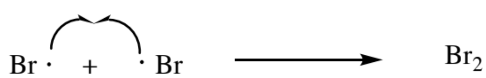
Termination Step: Radicals Recombine

-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)



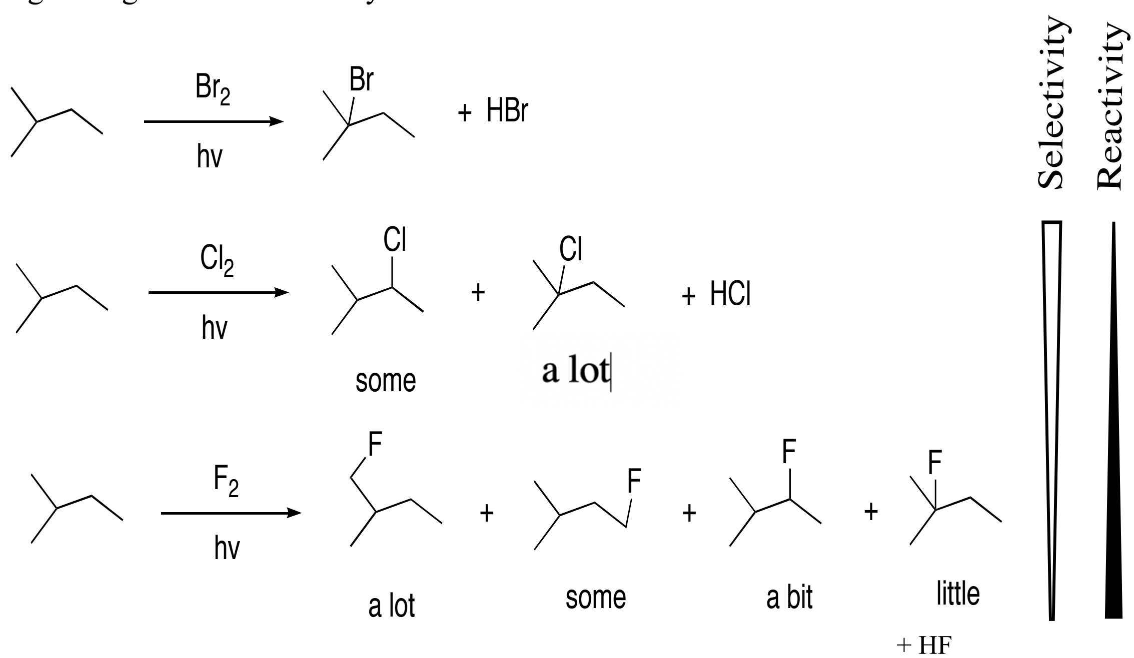
Hammond Postulate

More reactive, less selective

Less reactive, more selective

Reactivity and Selectivity (Hammond Postulate)

e.g. Halogenation of 2-methylbutane



I_2 does not react as above

Energy Diagrams of Halogenation Reactions

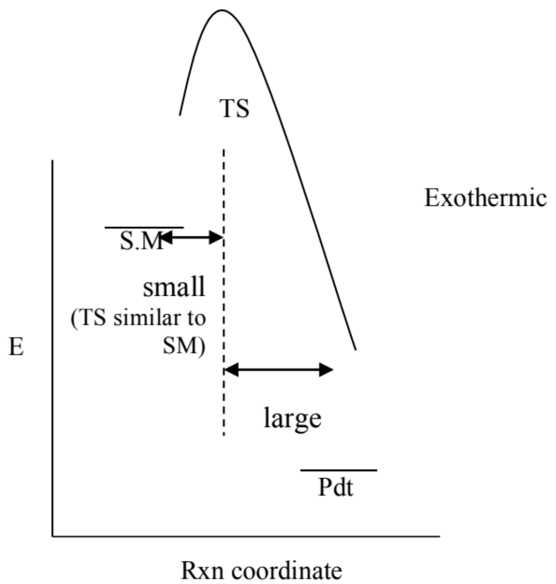
Note:

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

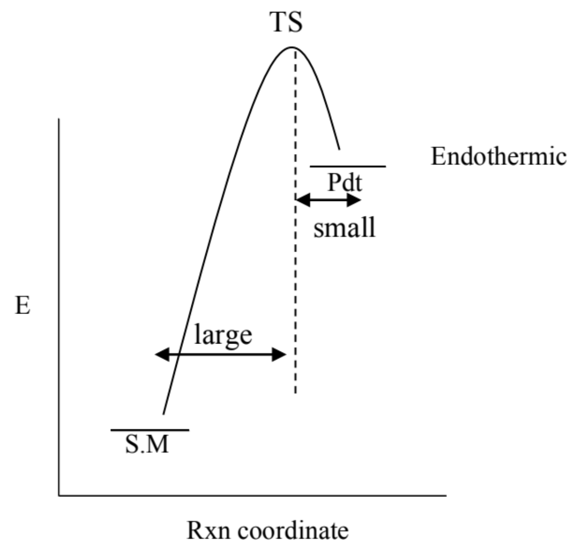
Endothermic T.S. resembles product
More selective because of a larger difference in Ea

Energy Diagrams for Halogenation Reactions

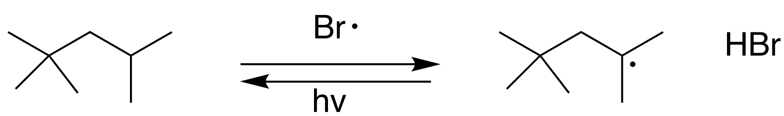
Fluorination (ΔH < 0)



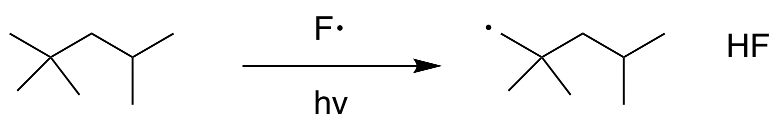
Bromination (ΔH > 0)



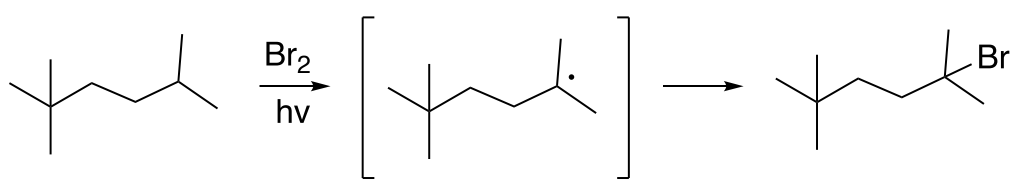
E = energy
TS = transition state
SM = starting material



Br_2 is less reactive, more selective, endothermic



F_2 is more reactive, less selective, exothermic



More exothermic, transition state resembles starting materials
More endothermic, transition state resembles the product

$R–H + X_2 \rightarrow R–X + XH$
Reactivity: $F_2 > Cl_2 > Br_2 >> I_2$ (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

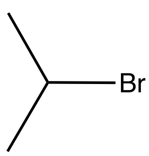
Naming of Alkyl Halides = Haloalkanes

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

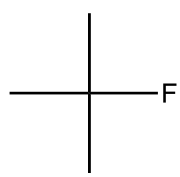
Structure and Nomenclature

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

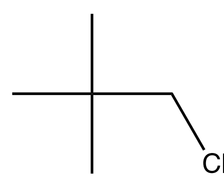
Examples:



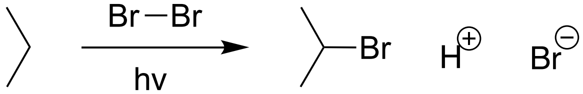
Isopropyl Bromide
2-Bromopropane



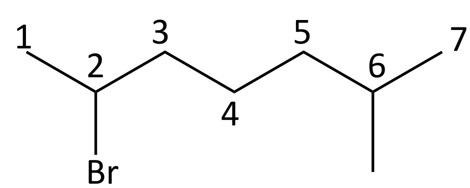
tert-Butyl fluoride
2-Fluoro-2-methylpropane



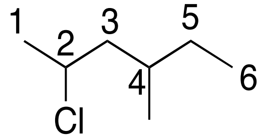
Neopentyl chloride
1-Chloro-2,2-dimethylpropane



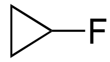
propane



2-bromo-6-methylheptane

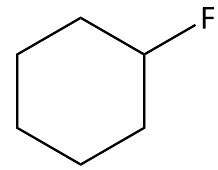


2 -chloro -4-methylhexane

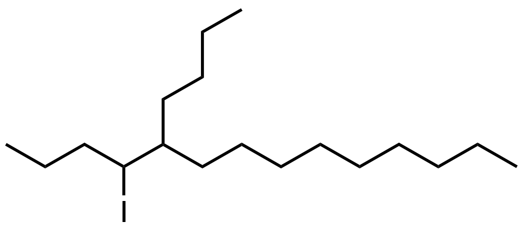


Fluorocyclopropane

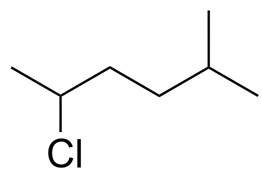
Cyclopropyl fluoride



cyclohexyl fluoride
1-fluorocyclohexane



5-Butyl-4-iodotetradecane

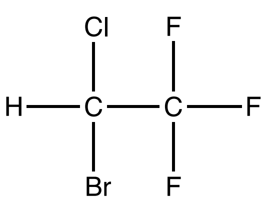


2-chloro-5-methylhexane

Note: Tert-Butyl = t-Butyl = tertiary Butyl

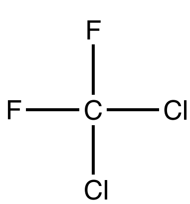
Applications of Haloalkanes

1.) Halothane (anesthetic)

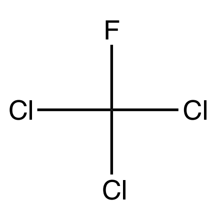


1,1,1-trifluoro-2-bromo-2-chloroethane

2.) Freon = refrigerants/coolants (react with ozone which protects us from strong UV)

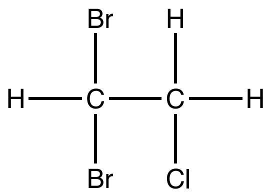


Freon 12



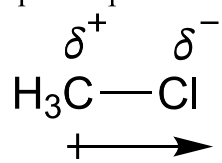
Freon 11

3.) 1,1-dibromo-2-chloroethane = male contraceptive (sperm count drops down to zero from 100 million/mL)



Physical Properties of Alkyl Halides:

- Governed primarily by dipole-dipole interactions, more polar than hydrocarbons/alkanes.



- High MP and BP relative to hydrocarbons of similar molecular weight
- Good solvents for organic compounds e.g. methylene chloride (CH_2Cl_2) and chloroform ($CHCl_3$) are very common.
- If % composition ≥ 65% halogen by weight, then more dense than water ($\rho > 1.0$ g/cm^3)
- Immiscible (insoluble) in H_2O, which floats on top of the halide