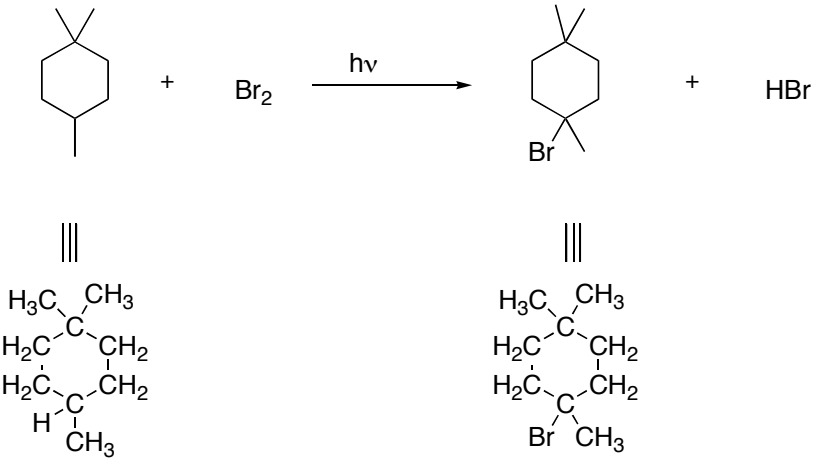
Stability of radicals:

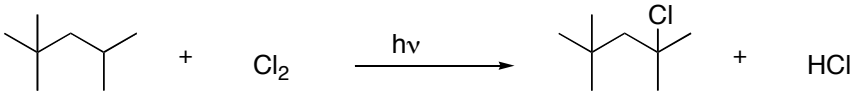
Increases with alkyl substitution.
Alkyl groups are polarizable and donate electrons to electron deficient sites.
Inductive effect: through single bonds

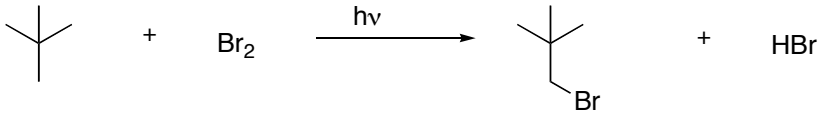
$\cdot CH_3$	<	$\cdot CH_2R$	<	$\cdot CHR_2$	<	$\cdot CR_3$
methyl radical (least stable)		primary radical		secondary radical		tertiary radical (most stable)

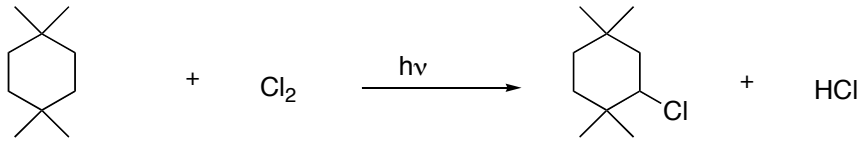
eg.

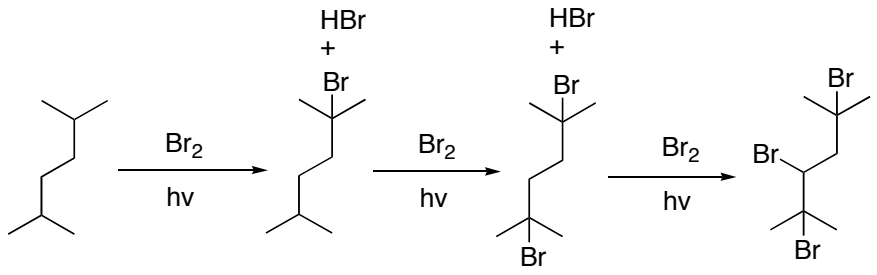


More examples:

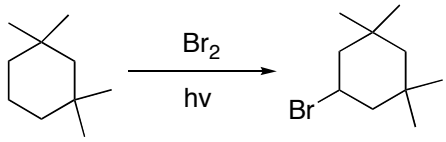
1. 

2. 

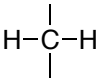
3. 



2, 5-dimethylhexane



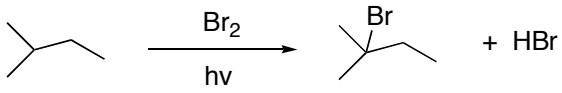
Note that the bromine is furthest from the methyl groups due to destabilizing steric interactions.

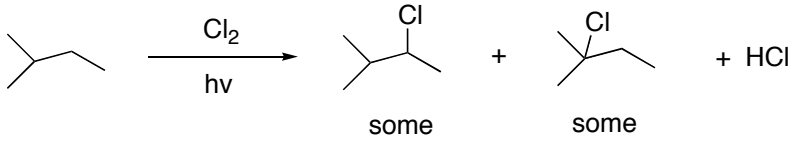


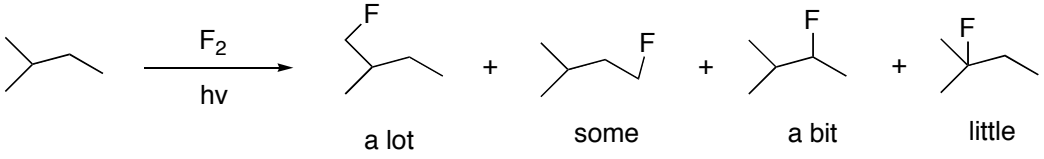
Methylene

Methine

Reactivity

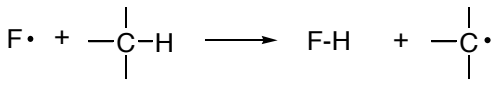






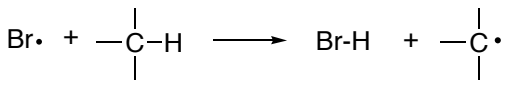
Reactivity

$F_2 > Cl_2 > Br_2 > I_2$



ΔH= -35kcal/mole

Exothermic



ΔH= +16kcal/mole

Endothermic

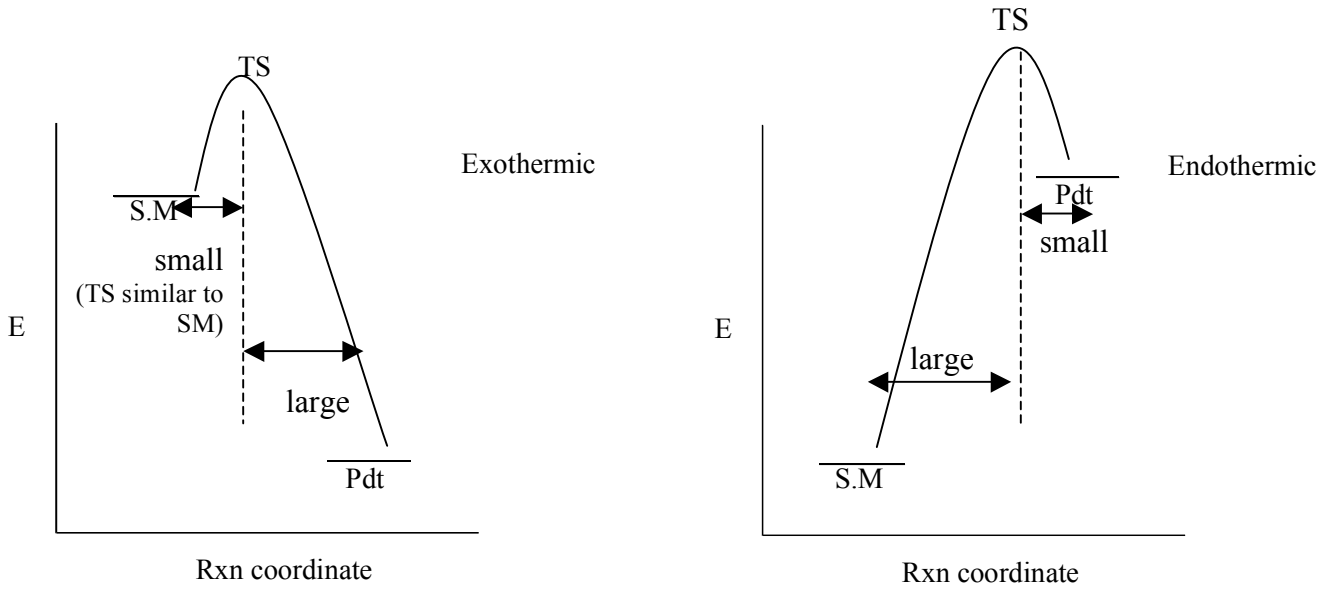
Br• > Cl• > F•

most selective — least selective

endothermic — exothermic

Hammond Postulate

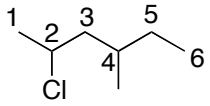
- The more exothermic a reaction, the more the transition state (TS) resembles the starting materials.
- The more endothermic a reaction, the more the TS resembles the product.



Alkyl Halides = haloalkanes

Structure and Nomenclature

1) Find longest chain with largest number of branches
2) Number from end so as to give 1st branch the lowest number
3) Name prefix with "Halo" (chloro, bromo, iodo, fluoro). Or name alkyl and add halide

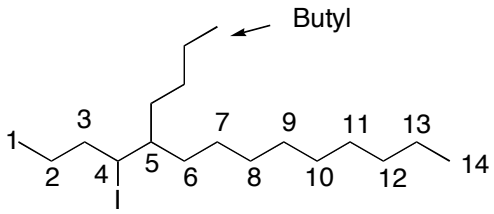


2 -chloro -4-methylhexane

Fluorocyclopropane

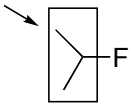
Cyclopropyl fluoride

look at atomic number



5-butyl-4-iodotetradecane

Isopropyl

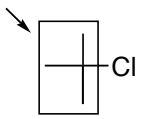


2-Fluoropropane

2-Propylfluoride

Isopropyl Fluoride

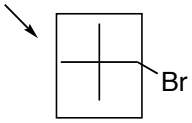
tert-Butyl



2-Chloro-2-methylpropane

tert-Butyl Chloride

Neopentyl



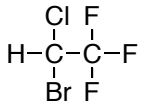
Neopentyl Bromide

1-Bromo-2,2-dimethylpropane

Properties of Haloalkanes

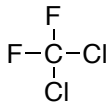
-
- if % composition > 65% halogen by weight, then more dense than water
- ρ = density > 1.0 g/cm^3 (water)
- immiscible (insoluble) in H_2O
- governed primarily by dipole-dipole interactions
- good solvents for organic compounds eg Dichloromethane and Chloroform
- High MP and BP relative to hydrocarbons of similar molecular weight

Ex) Halothane

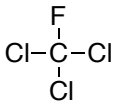


1,1,1-trifluoro-2-bromo-2-chloroethane

Ex) refrigerants

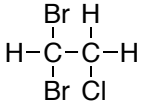


Freon 12



Freon 11

Ex)



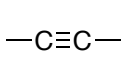
1,1-dibromo-2-chloroethane

In adult male, sperm count is typically 100million/mL - can be reduced to 0 by these antifertility agents

ALKENES AND ALKYNES

Alkenes and Alkynes – Term olefin comes from: oleum facere

↳ Olefin "oil" + "to make"

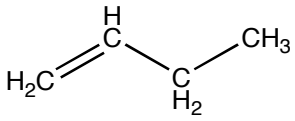


Alkene (olefin) Alkyne (acetylene)

Alkenes – structure and nomenclature

- find the longest chain with both ends of multiple bond within
- number from end to give first doubly bonded carbon lowest number
- drop –ane, add –ene
-

2-butene



1-butene