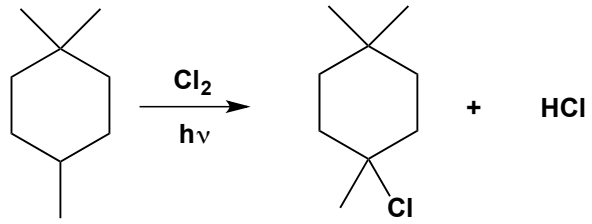
REVIEW:

Stability of radicals:

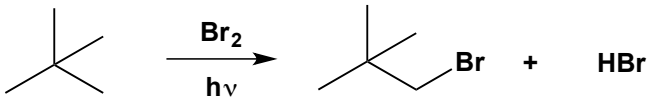
- Increases with alkyl substitution.
- Alkyl groups are polarizable and donate electron density (negative charge) to electron deficient sites.
- Inductive effect: through single bonds

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

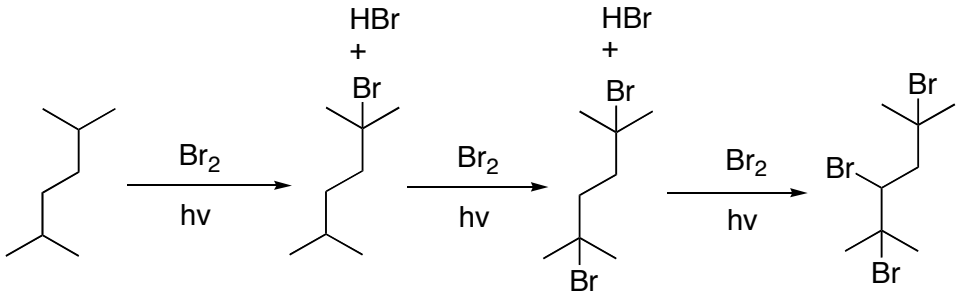
Examples:



1,1,4-trimethylcyclohexane

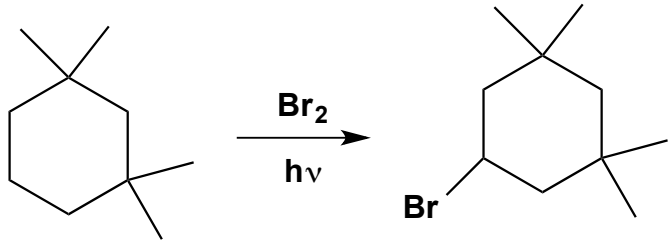


Neopentane
(2,2-dimethylpropane)



2, 5-dimethylhexane

1,1,3,3-tetramethylcyclohexane

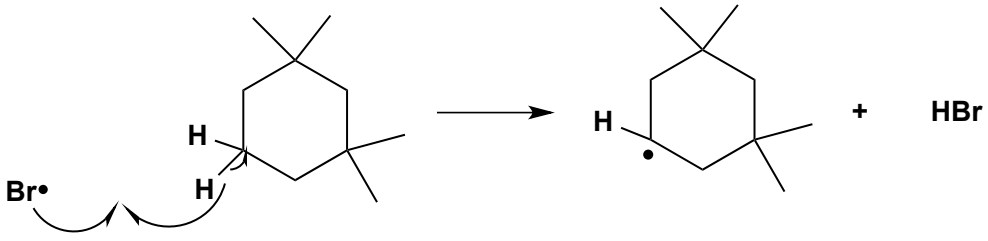


Note that the bromine is furthest from the methyl groups due to destabilizing steric interactions. Out of the methylene groups available, this one is the easiest for the bromine to access.

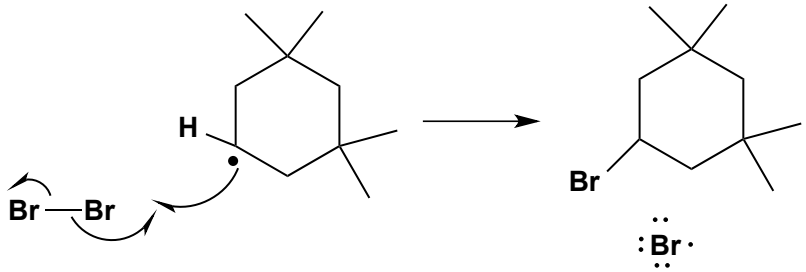
Mechanism of reaction of 1,1,3,3-tetramethylcyclohexane

Initiation

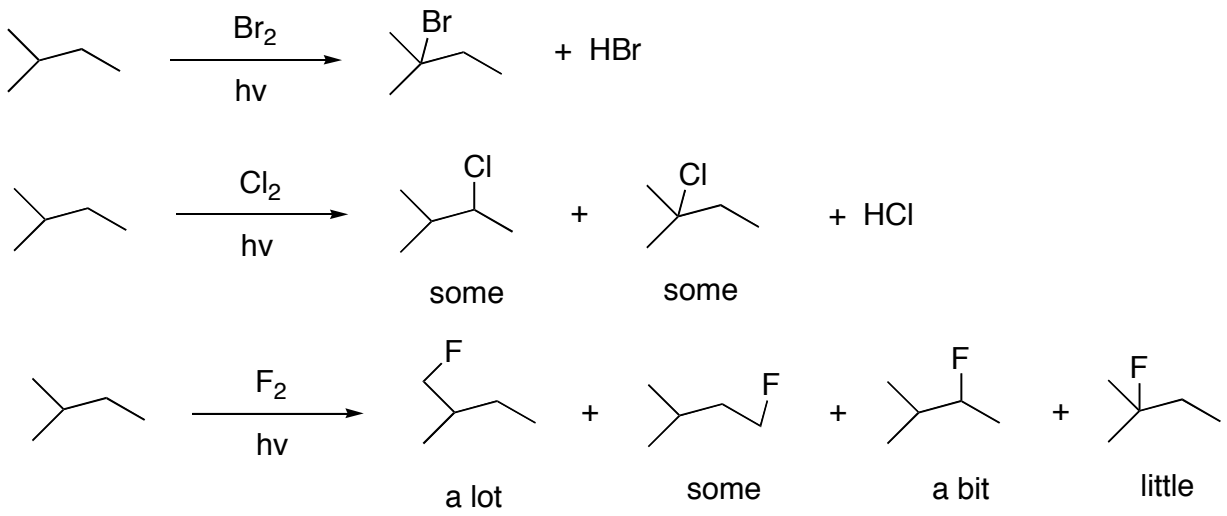
1st propagation step



2nd propagation step

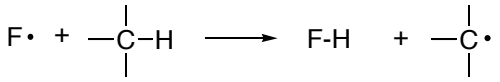


Reactivity and Selectivity (Hammond Postulate)

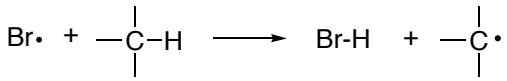


Reactivity

$F_2 > Cl_2 > Br_2 > I_2$ Iodine does not react



ΔH = -35 kcal/mole
Exothermic



ΔH = +16 kcal/mole
Endothermic

Br• > Cl• > F•

most selective — least selective

endothermic — exothermic

Bromine atom "searches" the molecule to create the most stable radical
Fluorine atom is small and feels the loss of an electron much more than bromine

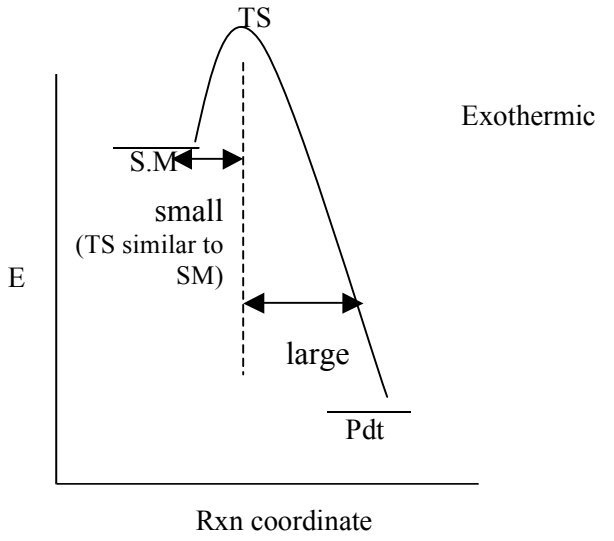
- Fluorine is less precise and reacts immediately

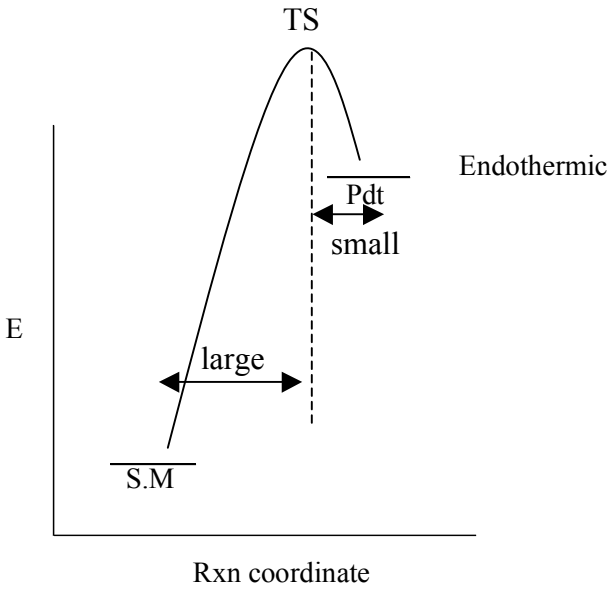
Hammond Postulate

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

Generally:

- More reactive radical → Less selective radical
- Less reactive radical → More selective radical

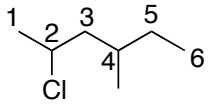




Alkyl Halides = Haloalkanes

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.

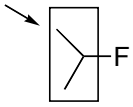


2 -chloro -4-methylhexane

Fluorocyclopropane

Cyclopropyl fluoride

Isopropyl

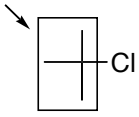


2-Fluoropropane

2-Propylfluoride

Isopropyl Fluoride

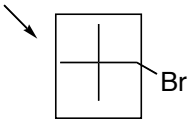
tert-Butyl



2-Chloro-2-methylpropane

tert-Butyl Chloride

Neopentyl



Neopentyl Bromide

1-Bromo-2,2-dimethylpropane