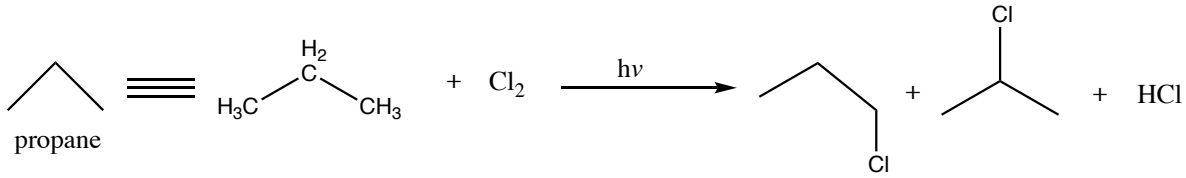
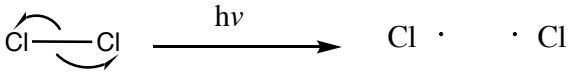
CHEM 261 October 02, 2017

REVIEW: Halogenation of Alkanes

Mechanism (Radical Substitution)
A. Chlorination of Propane

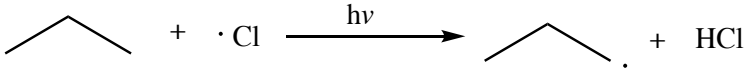


1. Initiation step

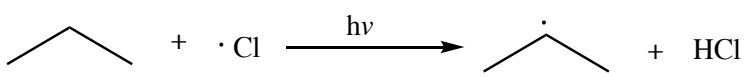


2. 1st Propagation step

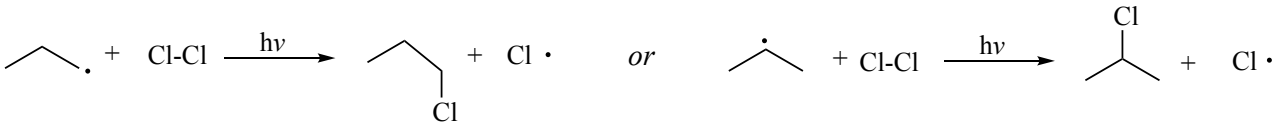
a. Primary radical formation



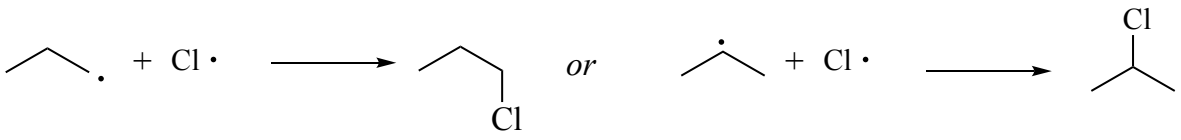
b. Secondary radical formation (more stable)

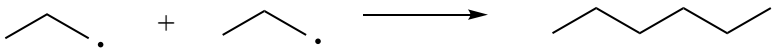


2. 2nd Propagation step

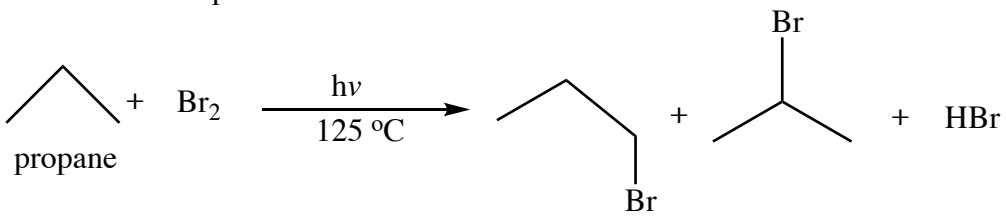


3. Termination steps



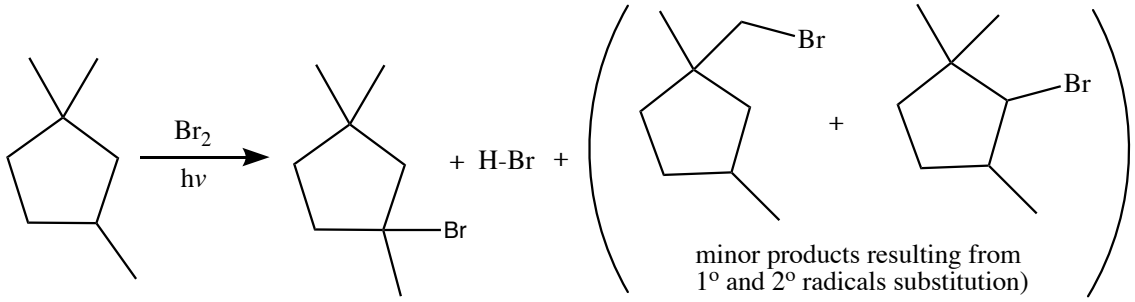


B. Bromination of Propane



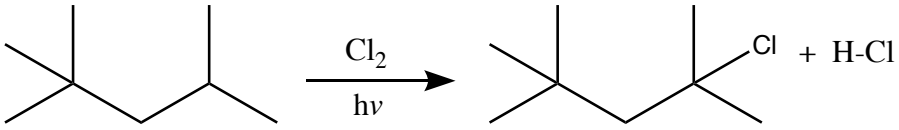
More Examples

A. 1,1,3-trimethylcyclopentane bromination



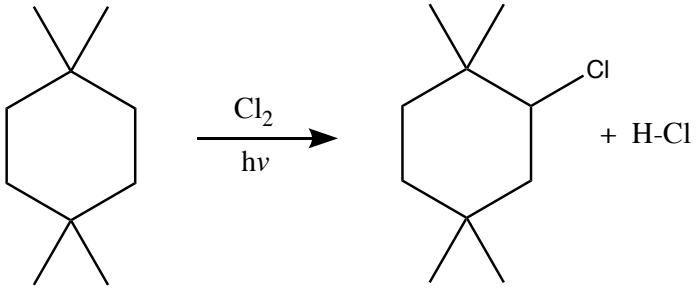
1,1,3-trimethylcyclopentane

B. 2,2,4-trimethylpentane chlorination



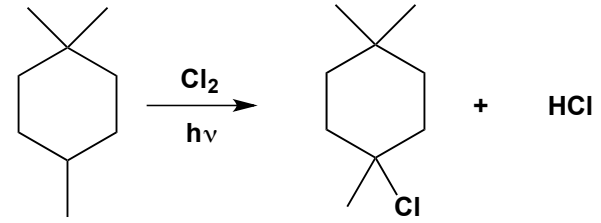
2,2,4-trimethylpentane

C. 1,1,4,4-tetramethylcyclopentane chlorination

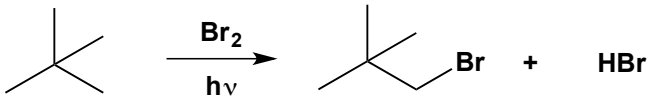


1,1,4,4-tetramethylcyclopentane

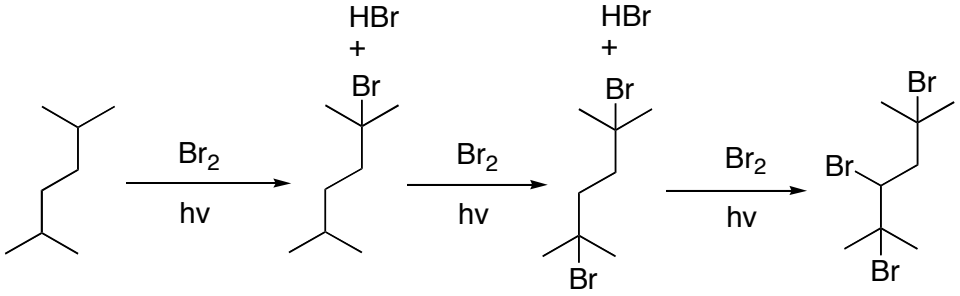
Additional examples for your reference:



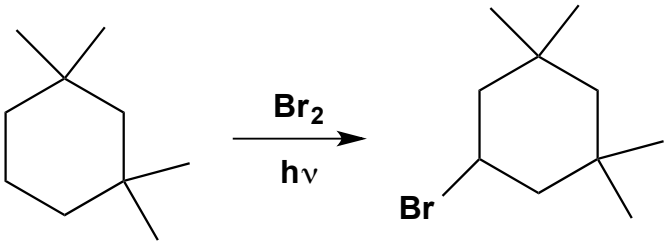
1,1,4-trimethylcyclohexane



Neopentane
(2,2-dimethylpropane)



2, 5-dimethylhexane

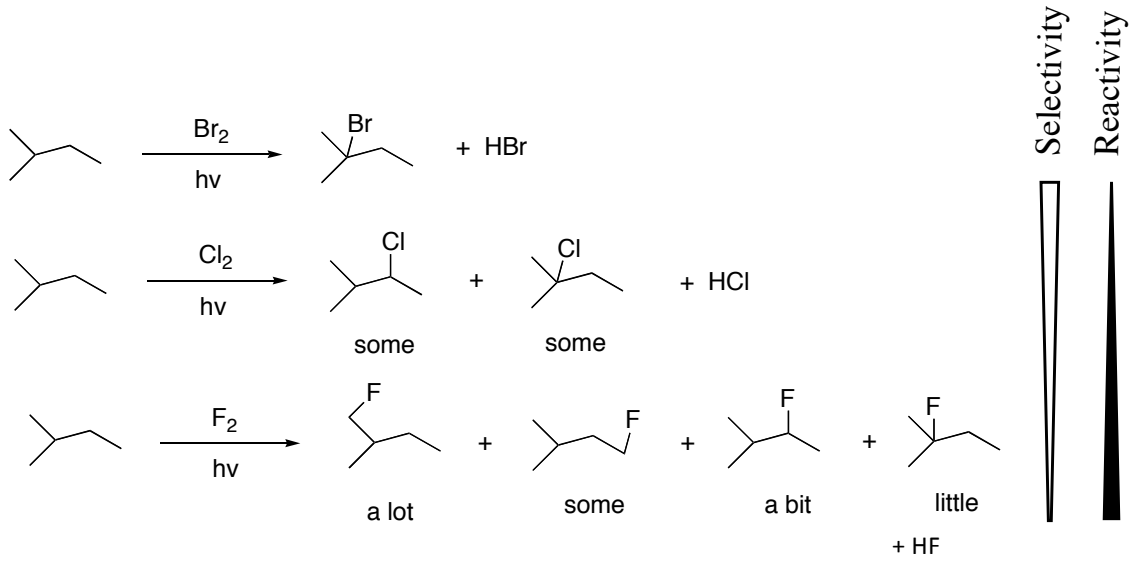


Note that the bromine is furthest from the methyl groups due to destabilizing steric interactions. Out of the methylene groups available, this one is the easiest for the bromine to access.

1,1,3,3-tetramethylcyclohexane

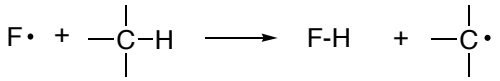
Reactivity and Selectivity (Hammond Postulate)

e.g. Halogenation of 2-methylbutane

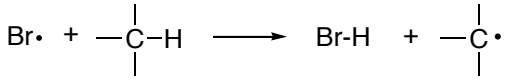


A. Reactivity TREND:

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



ΔH = -35 kcal/mole
Exothermic



ΔH = +16 kcal/mole
Endothermic

B. Selectivity TREND:

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