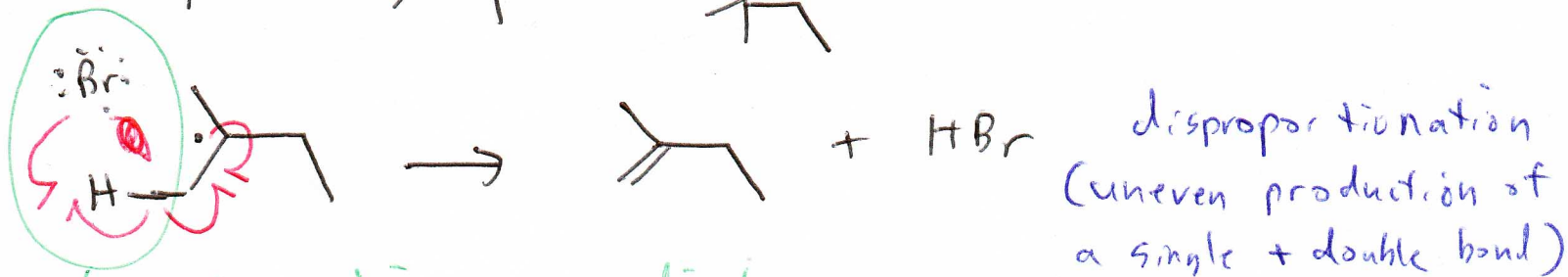
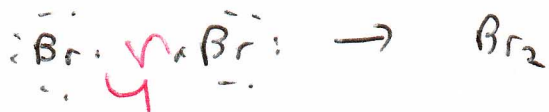
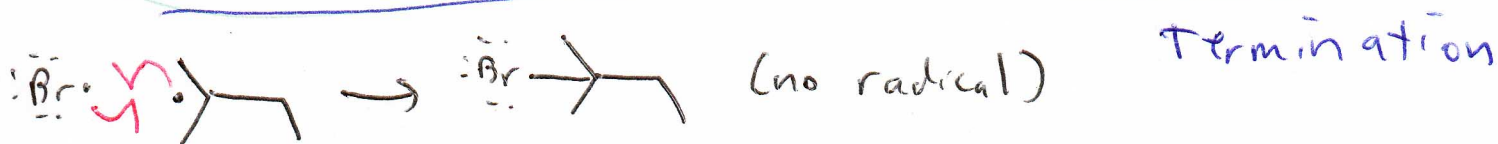
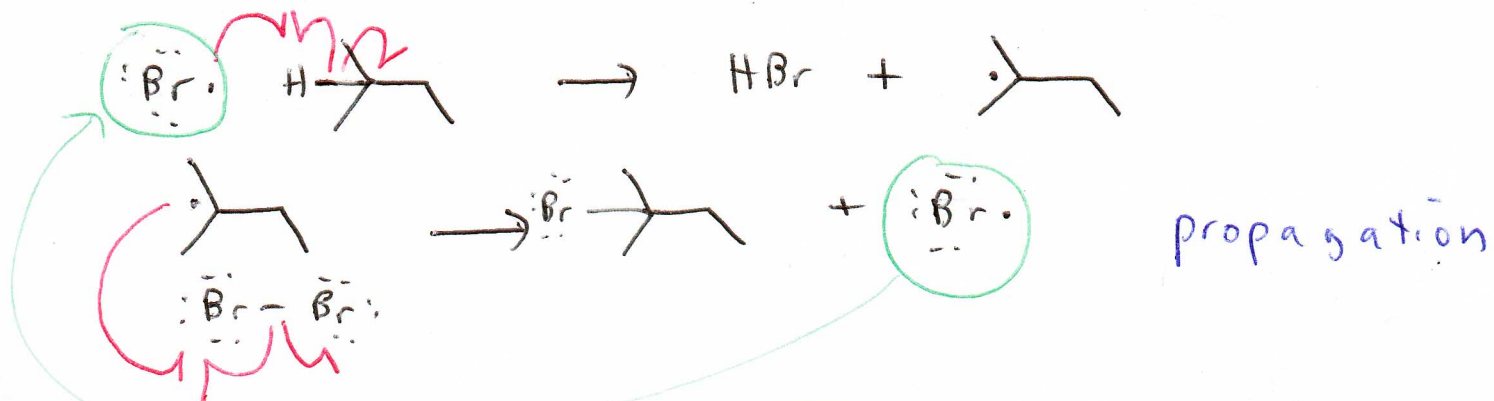
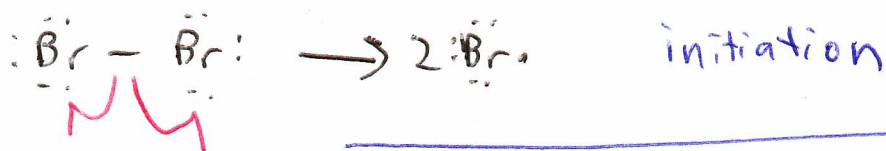


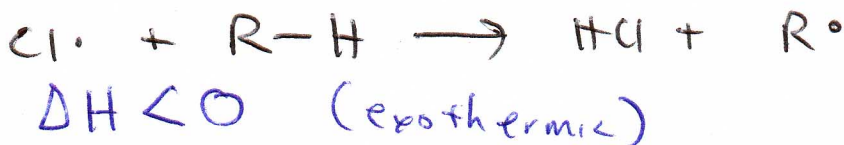
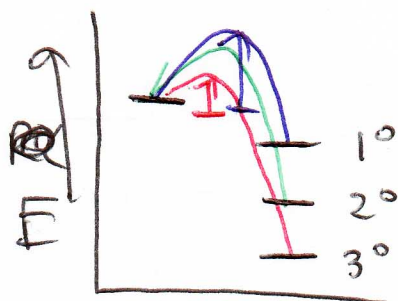
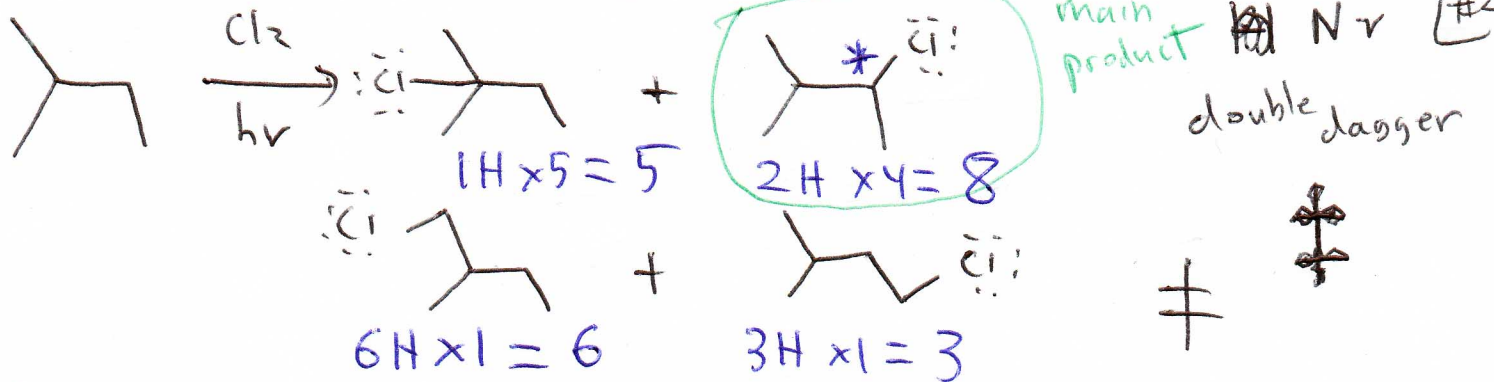
11/9/11 Radical Halogenation

#1

- 1) Synthetic utility alkane \rightarrow alkyl halide
- 2) Reagents Cl_2 or Br_2
- 3) Conditions $h\nu$ (UV light)
- 4) Mechanism
- 5) Stereochemistry
- 6) Regiochemistry



abstraction - a radical pulling H off a molecule



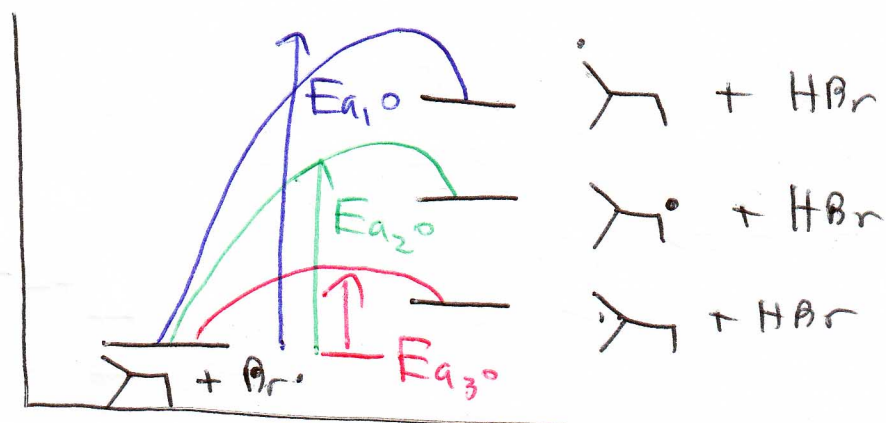
Hammond Postulate - The structure of the transition state more closely matches the structure of the product / reactant / intermediate that is closer in energy to the transition state.

In this case, since the \neq more closely resembles the reactant, there is not a huge difference in the activation energies for forming the 1° vs 2° vs 3° carbocations,

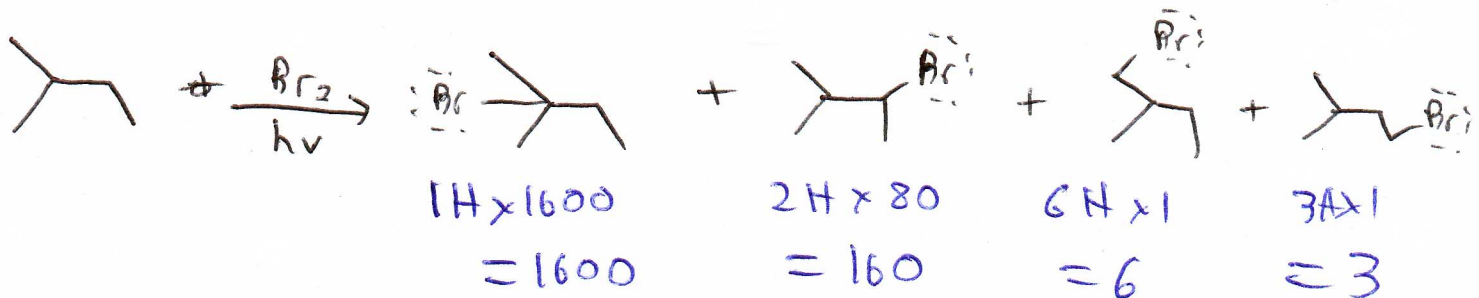
Relative reactivity $1^\circ : 2^\circ : 3^\circ$ hydrogen with $Cl\cdot \rightarrow 1 : 4 : 5$

Regiochemistry - In radical halogenation, every possible product (generated from every type of removable hydrogen) will form. The product distribution that forms depends on the number of hydrogens involved multiplied by the relative reactivity of that hydrogen.

Relative reactivity w/ Br· 1°:2°:3° → 1:80:1600 (#3)

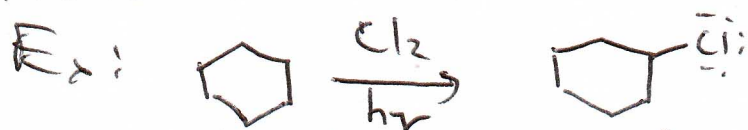


Since the transition state in this rxn step more closely resembles the product, there is a greater difference in the activation energies for the formation of a 1° vs 2° vs 3° radical.



When possible, bromine is used instead of chlorine because of its much greater regiochemical selectivity.

Chlorination is normally not used because of poorer selectivity, or if it is used, it is used on symmetric molecules.



Iodine is not used because the rxn Overall is endothermic → in light, alkyl iodides decompose.

Fluorine is not used because the overall rxn is #4
too exothermic, which results in there being almost
no difference in the activation energies for forming
different kinds of radicals

$1^\circ : 2^\circ : 3^\circ$

$1 : 1.2 : 1.4$