CONCEPT: RADICAL SELECTIVITY – QUALITATIVE

□ Selectivity is defined as the ability to only halogenate the carbons with most stable radical intermediates.

↑ Exothermic ≡ ↑ Non-selective ≡ ↑ Unhealthy

Fluorination:

- Overall ΔH^o = -432
- ***No useful*** radical fluorination reactions.

Chlorination:

- Overall ΔH^o = -101
- The only useful radical chlorinations are reactions with a single type of - H

Bromination:

- Overall ΔH^o = -26
- **The only useful** method for selectively halogenating alkanes

Iodination:

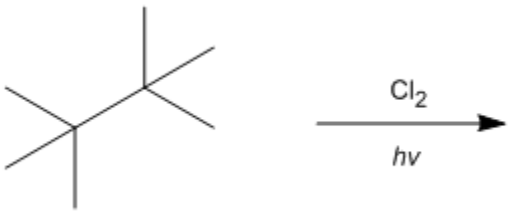
- Overall ΔH^o = +53
- Not a spontaneous, don't even try it.

Chiral Products are ALWAYS racemized

EXAMPLE: Draw the product of the following radical chlorinations. Would the following radical chlorinations be synthetically useful? (Yielding only one product).

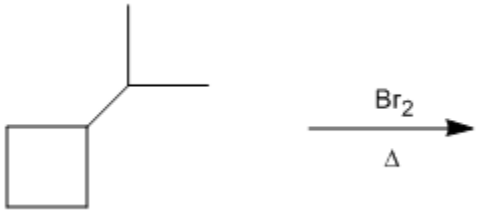
1)

2)



EXAMPLE: Predict the following monobrominated products of the following radical brominations:

a. 

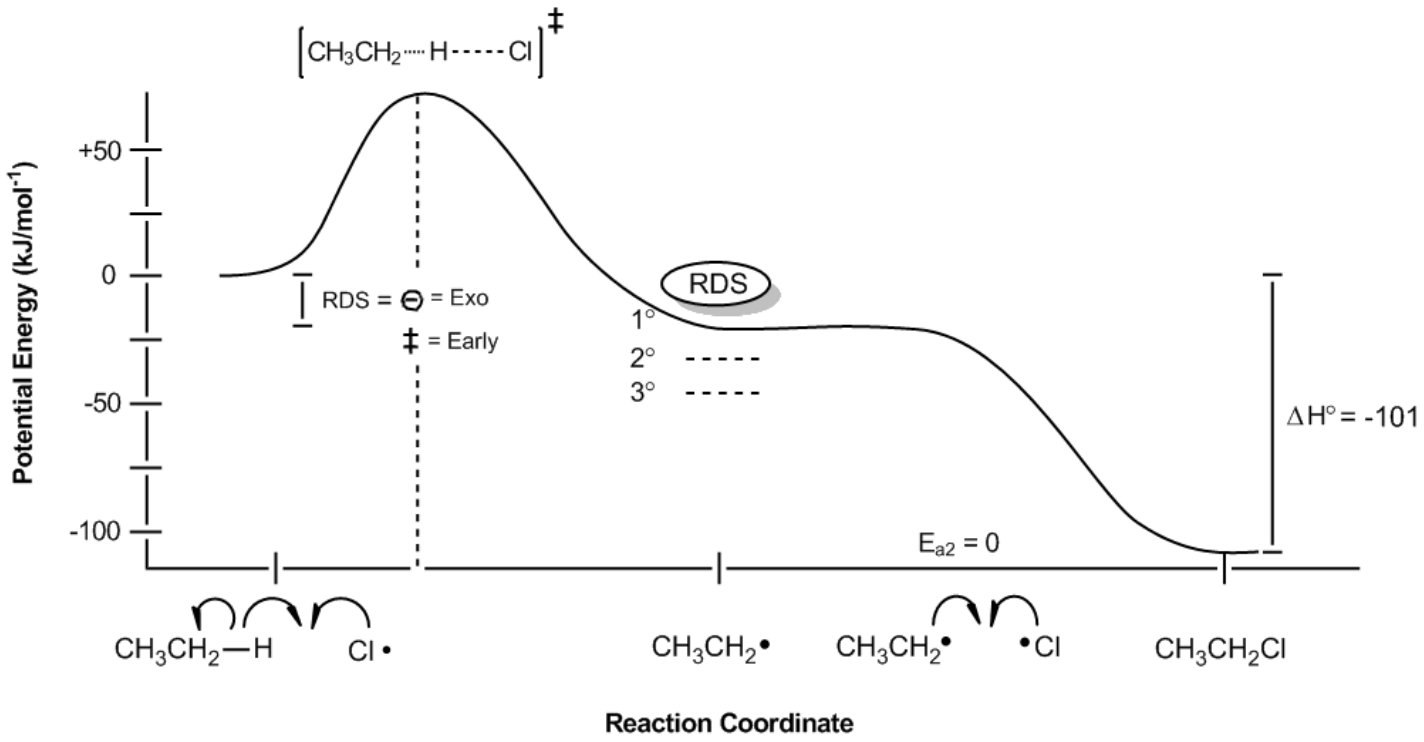
b. 

CONCEPT: RADICAL SELECTIVITY -- QUANTITATIVE

□ Selectivity is defined as the ability to only halogenate the carbons with most stable radical intermediates.

- The Hammond Postulate explains why halogen radicals have differing selectivities.

Radical Chlorination



Radical Bromination